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Definition, History, Discipline

1.1 Definition of Environmental Engineering

Environmental sciences strive to analyze and understand—by chemical and other methods—the influence of radiation (electromagnetic of various wavelengths, etc.), chemical compounds and yet other organisms on living matter and on those parts of Earth (crust, soil, upper lithosphere, hydrosphere, atmosphere) in which life occurs in an active form. In contrast, environmental engineering is meant to alter or exploit (environmental biotechnology, biological parts of sewage treatment system, etc.) these interactions to the benefit of humans and/or the environment. We shall see what this means. By biological activities, the above regions are profoundly changed; just consider chemical and climate effects of biogenic atmosphere components like O_2 , CH_4 , or the construction of vast coral reefs by organisms. *Environmental chemistry* deals with the “more chemical” features of this interaction and of processes which take part in the environment. It is the study of the sources, reactions, transport, effects and fates of chemical species in the air, soil and water environments, and the effect of human activity on these. *Environmental technology* is more the application of the environmental science and green chemistry to conserve the natural environment and resources, and to curb the negative impacts of human involvement. Sustainable development is the core of environmental technologies. This brings about the following definition of *environmental engineering*:

Environmental engineering is the technology concerned with the reduction of pollution, contamination and deterioration of the surroundings in which humans live, including environment and management of natural resources. This integrated management—beyond purification (waste or flue gas treatments)—includes reuse, recycling and recovery measures.

Accordingly, environmental engineering occurs at the interface of technical and environmental systems, and it requires a certain size of mass turnovers, even though the single devices may be fairly small if distributed among a multitude of individual pollution sources, like with catalytic exhaust gas converters.

Understanding chemical processes in the environment of course takes a sound knowledge of the array of compounds, ions and elements which are there, and of their distribution among the environmental compartments, which in turn controls

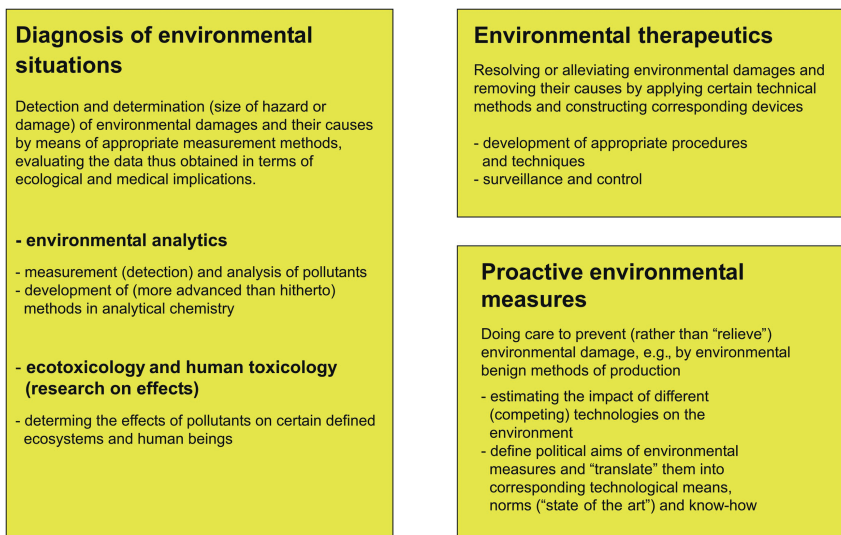


Figure 1.1 Diagnosis of environmental situations, environmental therapeutics and proactive environmental measures.

their exposure to secondary influences (e.g., UV irradiation, activation by chemisorption to, e.g., clay minerals). To obtain the corresponding information, lots of analytical data are required, that is, environmental analysis is warranted, while the secondary effects can only be described and evaluated concerning their implications for a realistic environmental setting by simulation experiments (Figure 1.1). Taken alone, it is rather pointless to determine the environmental half-life¹⁾ of some chemical species unless if one has sufficient additional information as to estimate whether some sink or source were apparently overlooked in modeling.

It is simple to demand more analytical data but, given the price of them, we are ever left with a pattern of sampling at rather distinct if not remote sites which must be linked by an extrapolation which fulfills the criteria of representative sampling. Expenditures for analytic data and therefore knowledge on environmental states being thus limited, we yet must go on to do "therapeutics", that is, the sanitation of obvious sources of pollution; and we must also abandon the use of substances which will cause hazards and damages only much later and at remote sites (global distillation causing PCB accumulation in the Arctic, ozone destruction, etc.). Hence proactive measures have to supplement cleaning up the more obvious mess. Surveillance and control—that is, analysis—are necessary in every stage of this development, to see whether the measures taken so far were successful.

1) The very term half-life includes the assumption that the decomposition processes are unimolecular, like photochemical decomposition via some

excited state or decomposition in adsorbed state or the cleaving agent is present in large excess (which holds for O₂ but not for any radical like OH, OCl, etc.).

Ecotoxicology thereby provides information which opens the view from mere chemical interactions and aspects of accumulation due to physicochemical properties to effects on single organisms and eventually to the effects these have for entire biocoenoses, causing members of one of many species to vanish, become less vital or conversely reproduce and spread by masses. The latter also can bring about chemical effects: the algae and cyanobacteria (phytoplankton) which form in response to eutrophication deliver *inter alia* chlorinated hydrocarbons which may attack ozone and certain poisons (red tides).

So let us now have a look at how we ran into the present situation and how far environmental engineering is a convincing response to demands produced by vast socioeconomic changes, some of which started more than 10000 years ago.

1.2 History and Development of Environmental Engineering

There is an extended prehistory of environmental engineering since people started reshaping their environs, which in turn required some measures to live so in an at least partially sustainable way.²⁾ The onset of agriculture in the Neolithic revolution enabled humans to gather in larger groups and to organize—now associated with agrarian areas—in correspondingly larger and less provisional settlements, distinguished by dwelling in stone houses now rather than mere wind-shelters (Koobi Fora), tents or cave entrances. The earliest of these which could be dubbed villages or even towns had a few hundred inhabitants each, like Lepenski Vir (Serbia, River Danube Iron Gate, site now inundated), Jericho (Palestinian Autonomous Territories), Çatal Hüyük (Turkey) or Poliochni (Lemnos Island, Greece; Tine and Traverso, 2001). Already then and there the increasing necessity to obtain wood, alter the landscape for agricultural purposes and later also to process ores caused damage to the local environment. In addition, people started to change their surroundings on some scale beyond felling trees, for example, when growing rice in man-made paddies—the earliest instance of “constructed wetlands” (given the first ones were located in the Lower Mekong area, beavers could not have given the idea for this innovation), with mining also dating back at least to the Mesolithic on various sites.

With larger extents of settlements and of corresponding production requirements, people had two choices:

- 1) Re-introducing migratory habits (slash and burn agriculture in a way replacing the former striding around with the game animals, on a somewhat longer timescale of relocation—a few years rather than months);
 - 2) More massively using and reshaping the local and regional environments (and to defend them, using the novel skills of metal technologies). These conflicts
- 2) Sustainable but not forever, yet lasting much beyond the present irreproducible resources, falling short of full replacement by regenerative matter and energy supplies.

are discussed, for example, in the Biblical stories from Genesis—Kain and Abel, and Abraham looking for a permanent place at which to live his personal culture and religion—and those conflicts which arose between Canaanites and semi-nomadic neighborhood tribes.

When they decided to do the latter, ecological problems associated with human activities were bound to aggravate even though the population used to increase but slowly then (in fact, the Neolithic revolution brought about a *decrease* in both average life expectancy and the chances of a child living to adulthood). In the other case nomads had to spread over vast territories, including use of force (the latest and most prominent example of a society of herdsman behaving like this being the medieval Mongolians under the Khans Cengis, Moengke and Ugedei, creating a huge yet ephemeral empire).

Either way, the environment received scars, and more than that (Thüry, 1995). Things got so bad that rulers were to set and enforce laws controlling the ways and sites of doing mining and ore processing, for example, while yet other innovations were to replace hitherto used “soft”, benign technologies of propulsion, travel and power supply (wind and water mills, animal muscle power, horse coaches, sailships, etc.) with more demanding—and polluting—ones like the steam engine and its derivatives. While “fuming” smokestacks were considered then—and often still even much after World War II—as an incarnation of progress and prosperity, people started to adopt the very technologies at hand for quite different purposes—and the same basic results of science—for improving the often dramatic, life-shortening state of environmental affairs, acknowledging there were no alternatives since now billions of humans (the first billion completed about 1830) were trying to make a living on this planet (Table 1.1).

International politics even today struggles with conflicts of distribution arising by this situation. Environmental technology—and environmental engineering as a operational branch feeding on it—thus became yet another facet of a “technology stalemate”, distinguished by the fact that about the same kinds of technologies were meant and employed to tackle the problems which hitherto contributed to creating them—except perhaps for electrical propulsion (which was not at all “green” then³⁾) and the use of chemical catalysts/filters for cleaning smoke gases and the like. Technology and environmental engineering thus kept a Janus face. In fact, neither a technology nor any kind of instrumental gear for (chemical) analysis was ever invented primarily for the purpose of improving the environment but taken from quite different ends and modified correspondingly, if at all: now soil cleaning is done using very much the same methods used in mining.

3) Consider the following facts: electrical energy storage—electricity taken from coal power plants rather than wind—took lots of highly toxic metals (Pb, Cd) then, if direct current was not even produced by releasing

toxic gases, like NO_x in the zinc/nitric acid/Pt battery, conversion efficiencies in motors were low (often, <10%), less than in mid-nineteenth century steam engines.

Table 1.1 A short description of the key cultural and socioeconomic changes, their environmental implications and the responses of rulers, society and scientists to tackle the problems.

Point of time/ period of culture	Event	Impact on environment	Remedy	Remarks
Mesolithic (≈25 000 years ago)	Extinction of big predators threatening and competing with stone-age hunters (cave and marsupial lion, giant monitor lizard <i>Megalania prisca</i>)	Trophic pyramid on solid land was essentially decapitated, changes in population structures aggravated by subsequent glaciation period		
Neolithic (≈10 000 years ago)	Revolution onset of agriculture, cattle-breeding, first larger permanent settlements, first production of synthetic structural materials (ceramics, metals/alloys of Pb, Cu, bronze)	Thorough change of land use, conflicts between hunter-gatherers and nomadic herdsmen here versus farmers there ^{a)}	Migration of tribes or other social units running into difficulties at stationary sites	
Ancient (3000–2000 years ago)	Large cities (Babylon, Rome, Alexandria), large-scale forest cutdowns, centralized infrastructures become labile in these large cities	Massive deforestation around large cities and all over the Mediterranean, peasant and native rebellions in Assur, Roman Empires		Consider (Hebraic) Bible, ancient eposes (Ilias, Edda) for recollections of the effects
Middle ages (5th–13th century)	Mass migration, opening new areas for agriculture, farming and cities by extensive deforestation, large-scale mining	Possibly climate change by deforestation	Ban of sulfide ore roasting in forests (14th century), official regulation of forest/wood use conflicts	
Industrialization (onset about 1730)	Invention of (direct-acting) steam engine, large-scale use of coal, extensive mining, development of large-scale chemistry and technology (factories replace small enterprises)	Greenhouse effect, decrease of rainwater pH, London-type smog, massive pollution of rivers by dumping chemical residues	Almost none, except for a reforestation program which essentially brought about monocultures of “cash crop” trees (spruce, beech, etc.), later definition of some protected areas; Yellowstone area as first National Park in the world	People thought about smoking stacks as a (the!) symbol of economical as well as social progress

(Continued)

Table 1.1 (Continued)

Point of time/ period of culture	Event	Impact on environment	Remedy	Remarks
Modern (since 20th century)	Megacities, chemical industry, N ₂ hydrogenation for fertilizers (Haber–Bosch process), problematic use of biocides, periodic oil spills, excessive whaling and fishery, individual traffic by cars and airplane use, production and discarding of “hard to biodegrade” polymers (“plastics”)	Eutrophication, partial destruction of marine trophic chains, effects of endocrine agents in aquatic and land environments, air pollution, increase of greenhouse effect, damage to ozone layer by Cl photochemistry	Ban of certain compounds (CFCs, TBT cation, polyhalogenated aromatics, biphenyls), introduction of car exhaust gas cleaning devices, attempts to replace fossil hydrocarbons for solvent and traction uses with biogenic (“green”) substances	Attitudes changed once effects became both regionally intolerable and impossible to look the other way (about 1970 ^{b)})

- a) See the Bible (Genesis 1) for an archetypical description of this conflict which still has the potential for manslaughter and war even today (Cain vs Abel).
- b) In (Western) Germany and all of central Europe, the first time the old consensus was replaced with another vision (“Let us have blue skies over River Ruhr once again!”), a plea for different ways of essentially post-industrial, post-mining living in an old pit area, was put forward during the 1961 Bundestag election campaign of Willy Brandt (Social Democrats; election rally at Essen, 28th April 1961). The Greens appeared in the late 1970s.

Environmental sciences thus are secondary in their development, as also is evidenced by the times when concepts now considered to be key terms were introduced in to the literature:

Ecology	(Haeckel, 1866; Wallace, 1876; Junge, 1885)
Environment	(rather than “Außenwelt;” Uexküll, 1909)
Biogeochemistry	(Vernadsky, in the 1920s)
Ecosystems	(in the 1930s)
Geoecology	(in English, rather “landscape ecology”, encompassing most sciences concerned with understanding and improving the environmental status; Troll about 1935)
Ecotoxicology	(Truhaut, 1969)

So it is a fairly recent approach, things becoming more disturbing when, for example, you compare the discussions about future ways of car propulsion (then, steam, or internal combustion engine or electric) in the first decade of the twentieth century to that of today—comparison often is really disgusting here! In many cases the actual impact of innovations in environmental engineering does depend less on what is technologically feasible at a given point of time—or at least appears to be so

disregarding limitations, for example, of catalyst resources⁴⁾—and more on political decisions. So the public recognition that there is some technology at hand to overcome a certain challenge or control a given pollutant—the key topic of applied environmental engineering—does not at all suffice. Rather, an environmental engineer has to consider aspects of political will and acceptance also: if nobody wants to have large-scale wind energy power plants or nuclear reactors “in his/her backyard” (or are afraid of the latter or of possible leaks in CO₂ deposition), it is outright futile to argue how much CO₂ emissions could be avoided or “passivated” by these technologies per MWyear (megawatts × years). Once people staunchly disagree on the very issue it becomes impossible to alter environmentally pertinent modes of behavior or supply strategies on relevant scales, at least not in democratic societies.

Environment contains hardly numerable different chemical species; in atmosphere alone some 70 compounds—excluding radicals and other short-lived intermediates—were detected and quantified so far. In the very moment analytical methods to determine parameters such as pH, redox potential and so on are used in the “open” environment, they will make their way into both methodology and thinking in environmental sciences. As a result, concepts from chemistry and (later on) cybernetics, systems sciences are going to be transferred into environmental sciences for some 170 years now at least, beginning with Liebig’s 1840 famous *Agrikulturchemie* (agricultural chemistry) and Schoenbein’s pioneering work on atmospheric chemistry, including discovery and atmospheric determination of the ambient oxidant ozone. Some observations, including detections of elements oxygen and nitrogen, and giving names to them according to their effects on (aerobic) organisms in pure state [for nitrogen, in German = *Stickstoff* (asphyxiating agent), in French = *azote* (not supporting life)] even date back much farther into the eighteenth century.

Examples of this conceptual “spillover” to the benefit of environment and its understanding include:

- Theory of chemical structures, implying/postulating that, most notably in isomeric compounds such as glycine and nitroethane or (Liebig’s classical) cyanate/fulminate couple, the unlike spatial arrangement of atoms and presence/absence of certain functional groups will bring about quite different physical and chemical properties (reactivity, toxicity, modes of decomposition) of otherwise identical chemical substances;
 - Ionic theory of electrolytic conductivity (most important for aquatic organisms which will often reproduce only within a given narrow range of conductivities);
- 4) For example, known and presumed platinum group metal (PGM) deposits would never suffice to endow all the cars presumably bought by Chinese or Indian citizens in the next 15 or 20 years to come with catalytic converters—let alone produce hydrocarbon- or alcohol-converting fuel cells for propelling most of them—and known amounts of lithium (Bolivia, Chile, Afghanistan, etc.) would also fall far short of electric car battery demands then. Accordingly both storage and conversion and exhaust gas purification techniques require much re-consideration for a large-scale application indeed (unlike with platinum group metals, Li extraction from seawater might prove feasible).

- Involvement of radical chains or ions in reaction mechanisms;
- Coordination chemistry (bioinorganic chemistry in life sciences as soon as essentiality of metal ions was linked to their forming catalytically active complexes inside proteins);
- Cybernetic systems analysis;
- Feedback patterns.

Actually, by proving there were no chemical elements whatsoever in living beings other than those already detected outside of them, biochemical and environmental analysis gave the final blow to vitalism, after Wöhler's demonstration that compounds like urea or oxalic acid could be prepared also by man rather than inside living creatures: biology, biochemistry, biophysics adhere to the same (and no additional⁵⁾) laws of nature as physics and non-biological chemistry do. Even after abandoning the vitalist assumption of particular rules life would follow, most (potential) environmental scientists still hesitated to transfer the rules and laws of physics and chemistry to systems shaped by biological activity mainly to a full scale. Much time after running the risk to be accused of adhering to either "materialistic" or "idealistic" prepositions (depending on which side of the former Iron Curtain you happened to grow up, live and work) came to an end, this reluctant attitude still poses obstacles to both understanding environmental processes and doing practical, efficient protection measures. In addition, education—starting at school at age six—suffers from people being reluctant (and often hostile) to link observations from different areas to each other, rather dealing with them as if they were completely isolated and independent of each other. For example, a class could have 45 min of chemistry, then 45 min of sports, music or some language, then yet another 45 min (topically unrelated again) of biology and so on. Thus young people are (often permanently) misshaped in their thinking and corresponding attitudes.

In a similar way, each model designed to describe some complicated system—be it an environmental compartment such as air, a biocenosis, an ecosystem or "just" a single organism—both stresses and neglects certain (mostly many) aspects of it. Both mere description and operational approaches, say, environmental biochemistry and environmental engineering, suffer from this likewise, the latter often even more strongly. Consider an example from medicine to understand this: there is a case of massive cardiac arrhythmia, possibly threatening the patient's life and anyway causing deep sorrows to him/her, going to be tackled by specialists from different areas of medicine. Psychologists will try to "understand" which circumstances caused the condition now manifest as physical illness while a cardiologist might try to fix the problem in and by treating the muscle itself, the former possibly suggesting family therapy while the latter might implant a cardiac

5) In fact, Fränzle (2010) undertook to analyze biochemistry, biocatalysis and reproduction along very basic physicochemical rules concerning structural complexity and

chemical feedback, unveiling some principal limiting conditions for life—on whatever chemical basis—to operate and on the establishment of essentiality.

pacemaker. Likewise an environmental chemist is going to address, correct and fix other features of some impaired environmental system than people stressing aims of “landscape quality” –with the latter working in a manner quite as “scientific” also! Returning to the former example, neuromyology and psychosomatics deal with different scales of embedding phenomena (the entire body or even the social surroundings vs the sinus node of the heart), quite like in the latter (from molecules to landscape dimensions).

Either approach is fully justified and also important: providing electrical stimuli may be pivotal to keep the patient alive even if the infection disease or personal conflict underlying the heart problem were neither diagnosed nor resolved so far. Quite similarly it is impossible to meet ambitious ends concerning landscape quality as long as the corresponding parts of the environment are subject to massive chemical burdens. Rather than considering one approach “better” or “worse”, we should acknowledge there are different –if not complementary– options which draw upon various different ways to analyze a given environmental problem.

Thus, one can actually take notions of esthetical and sensorial perturbations as warning signals, prompting us to tackle a poor situation [vegetation which succumbs to pollution across vast areas is considered “ugly”, as are mass spreadings of a few pollution-resistant species (nettle, algal or cyanobacterial blooms), while polluted air and water reduce both physical and psychical well-being of people exposed]. Luckily, man is not a particular sensitive bioindicator; however, detrimental effects of pollutants toward vegetation were noticed early, correctly linking these to human activities, especially mining. For examples from old history, consider remarks on damage to forestry and lichens in mining areas.

Pliny the Elder already noticed that mining of certain ores released gases which damage vegetation, the production of such gases being related to the presence of sulfur (and its oxidation as we now know). The active plant poison mainly is SO_2 , possibly with admixtures and co-effects due to carbonyl sulfide (COS). The above observations prompted rulers (kings, dukes, bishops) in possession of large forest areas already in the Middle Ages to outlaw mining and ore processing inside either forests or human settlements. In addition, lichens were noticed becoming rarer and eventually vanishing in industrialized, heavily populated regions such as London during the nineteenth century (i.e., subsequent to the industrial revolution and thus vastly increased coal combustion rates). This once again was interpreted (correctly) to inform of increasing air pollution. From there, the topic soon made its way into popular literature, consider the numerous allusions to London “fog” (rather being smog in a very pronounced form) and its role in the plot of A.C. Doyle’s criminal novels of Sherlock Holmes⁶⁾ and his detective work.

As for environmental chemistry between about 1850 and 1940, some men should be mentioned who drove their brilliant and fundamental works on organic and physical chemistry, spectroscopy (IR, etc.), reaction kinetics and geochemistry

6) Most likely, a friend of Doyle’s who was one of the pioneers of both forensic and environmental analysis, J. Norman Collie (1859–1942), and who additionally claimed

to have discovered noble gas neon before Ramsay did, was the historic figure after whom Holmes was depicted (Emsley, 2001).

even further to investigate environmental implications of their discoveries, namely Christian S. Schoenbein, Svante Arrhenius (1903 Nobel laureate in chemistry), Volodymyr Vernadsky, Sidney Chapman and the Odum brothers. (This is not to suggest that women did no eminent work in the development of environmental chemistry and engineering, respectively, but apparently it is fair to state that it was less obvious in terms of some “inter-sex competition” than in, say, mathematics or radiochemistry/nuclear chemistry.)

C.S. *Schoenbein*, the father of atmospheric chemistry, also coined the term “geochemistry” (Kabata-Pendias, 2001). In 1840, he first produced and discovered ozone (O_3), later (1858) detecting it in tropospheric air also by iodide oxidation during balloon ascents, then finding yet other photooxidants such as hydrogen peroxide in rainwater. As for environmental engineering, it should be noted that he, at the same time (1839) but completely independently from Grove, developed the first *fuel cells*⁷⁾ using H_2 (Pehnt, 2002), while in applied organic chemistry he became famous as the inventor of “nitrocellulose” (rather, cellulose nitrate polyester) explosive.



Christian Schönbein (1799–1868)

- 7) From the viewpoint of environmental engineering, and given the almost practical state of affairs reached in the late 1830s concerning electropulsion of both cars and little ships, it is outright tragical that the first successes by Schoenbein and Grove using dihydrogen were not taken further to achieve ethanol electroprocessing by Pt mediator electrodes; instead it was tried (in vain) to achieve fuel cell electrocombustion of coal (which succeeded just a few years ago) from then on much into the twentieth century. Such activated Pt surfaces, used by both Grove and Schoenbein, also were already then state of the art, for example, in zinc/nitric acid piles providing kilowatt power outputs. This would straightforwardly have provided efficient fuel cells operating on liquid biogenic fuels, rather than very heavy Pb accumulators or primary elements. But for this misdecision, fuel cell/electromotor propulsion systems would have successfully competed against the steam engine in propulsion very soon afterwards.

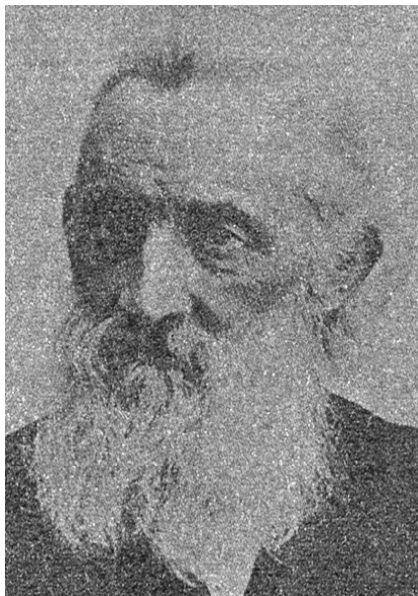
Being among the pioneers of IR spectroscopy, and following earlier suggestions by Tyndall (1872) concerning atmospheric and climate drawbacks of IR absorption by increasing CO₂ in the air, Svante Arrhenius pursued the question of climate effects of this CO₂ enrichment from 1896 onwards before quite unrelated work—advancing the ion theory of salts and its drawbacks for producing electrically conductive solutions and melts—won him a Nobel in 1903. Arrhenius's and Högbom's 1896 work on the greenhouse effect (Arrhenius, 1896) included all estimates of its anthropogenic share (“radiative forcing”) from IR spectroscopy, expected extent of global warming and speculated about counter-acting climate secondary effects, such as changes of rainfall. Considerable public interest was arised by their corresponding demand to limit the burn rates of coal which had already by then caused massive environmental problems by SO₂ releases. In addition Arrhenius dealt with biochemical problems such as modes/mechanisms of toxin–antidote interactions or the chemistry of digestion. His formula to calculate activation energies yielded deepened insight into reaction mechanisms and to activation of chemical reactions.



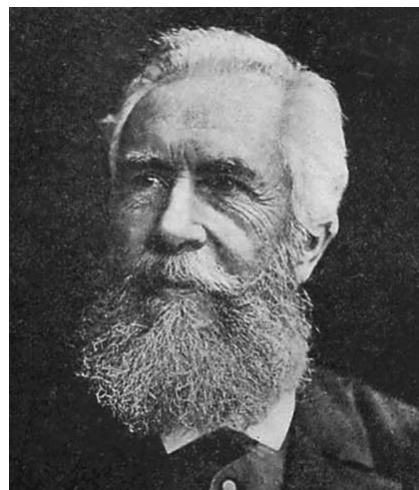
Svante A. Arrhenius (1859–1927)

The ecological paradigm, although explicitly based on considerations of matter and energy fluxes and balances, which was brought into biology by Junge and Haeckel about 1870, strangely was treated for quite a while as if entirely unrelated to chemistry. Junge (1885) discussed a community of organisms in its interactions considering a pond (*Der Dorfteich als Lebensgemeinschaft*—“a village pond seen as a community of living beings”). Haeckel defined ecology to describe or be *gesamte Wissenschaft von den Beziehungen des Organismus zur umgebenden Außenwelt*—“the holistic science covering the organism–outer world relations” [the term

environment (*Umwelt*) as opposed to outer world/surroundings (*Außenwelt*) was coined only much later, in 1909]. This way to cover and analyze outer relationships of an organism necessarily includes metabolic exchange due to breathing and feeding. This strongly suggests now to focus on exchanges of oxygen and CO₂ among fishes and water plants as a chemical process crucial for this biocenosis but the pioneers did not, then, possibly feeling the difficulties they would run into (without isotopic markers or the like at hand). Rather soon after Liebig had paved the way for this kind of reasoning by investigating the chemical processes in soil and in the soil–plant system, providing useful insight for agriculture, some chemical formulation of the ecological paradigm might be thought the more straightforward as aquatic chemistry was rather advanced already then. Accordingly one might anticipate chemical ways of thinking soon to be introduced into the emerging science of ecology, like they did in physiology, but this did not happen until some 40 years later when Alfred *Lotka* and Vito *Volterra* did use chemical models (borrowed from radical chain chemistry) to model population dynamics of two species coupled by predator–prey relationships. Soon after, beginning in 1916, Volodymyr (the original Ukrainian name, usually transliterated–Russian–as “Vladimir”) Ivanovich Vernadsky started integrating the views of biochemistry, metabolism and geochemical cycles on Earth which is influenced by biological activity, creating yet other feedback loops. Such feedback systems are capable of unprecedented dynamics, including oscillations⁸⁾ as Lotka pointed out, creating a



Friedrich Junge
(1832–1905)



Ernst H. Haeckel
(1834–1919)

8) Among chemical oscillators, however, it turned out to be very difficult to produce any which works along Lotka’s rather simple feedback structure.



Alfred Lotka
(1880–1949)



Vito Volterra
(1860–1940)

new paradigm again, that of feedback control and cybernetics, augmented by the onset of electronics, both theoretical and technical (Turing, Wiener, Forrester) which in turn provided the means to analyze such systems efficiently (Forrester modeling, which soon made its way into ecology also), with the key parts of computers being prone to feedback control and amplification themselves (triode, transistor).

By using this feedback reasoning on the integration of metabolism into geochemistry, V.I. Vernadsky became the founder of *biogeochemistry* (this term being his, also), producing fundamental work on the involvement of living beings into Earthly matter cycles together with his school [now the Vernadsky Institute of Russian (formerly Soviet⁹⁾) Academy of Sciences]. Vernadsky's point of view was never restricted to single ecosystems but he covered the entire Earth from the very beginning, for example, postulating that biological evolution was (also) about introducing all the accessible atoms into biochemistry. He went so far as to consider the metasystem consisting of living matter and its environment as alive by itself. His focus on concentration of elements by metabolism of whatever organisms is essential to ideas and approaches like bioremediation, biomining and biological waste treatment now. His "basic biogeochemical rules" (he even called them . . . laws; Levit, 2001) refer to the fact that living beings, by reproducing and spreading, continue to absorb resources from all three environmental

9) By the way, Vernadsky also was (in 1918) the founder of the *Ukrainian Academy of Sciences*; and it is not quite clear why he eventually returned to Stalinist USSR in late

1927 after doing research and teaching in the West for about five years, including Berlin, Paris and the United States of America.

compartments to an increasing extent, partly binding them for about a lifetime, partly passing them through rapidly. The amounts of elements involved in such biogeochemical cycles used to be much larger than turnover by mining or similar anthropogenic activities until recently. It must be noted, however, that even now only a few elements in the biosphere are retained by living beings to a share of 10% or more (essential elements P, Zn, Cu; and highly toxic trace metal Be) while the biosphere represents some 1–2% of C, Fe, Mn available across the biosphere only and much less of crucial elements such as N, S or Mg.

A seminal work, never to be reproduced for any other larger part of Earth's solid surfaces, by Vernadsky and his co-workers/successors is his "Atlas of biogeochemical provinces of USSR", begun in 1943 and completed by Vinogradov. It covers that huge area of some 15% of Earth's solid surface completely and often highly resolved, except for Tajikistan and the Arctic coasts. Therein, "deviations" of levels of certain elements are linked by epidemiology to diseases of man and animals, and to the abundances of plant and animal species, some of them known to accumulate or at least tolerate substantial concentrations of these elements. This provides information pertinent to both health protection, toxicology and ecology. Using the remarkably high spatial resolution, for example, in the Caucasus areas allowed a definition of the needs and strategies for the remediation of polluted soils, ground and surface waters. Biogeochemical provinces as such may also be distinguished by and named after essential elements like manganese or zinc.



Vladimir Ivanowitsch Vernadsky (1863–1945)

Sydney *Chapman* originally was a mathematician but became intrigued with physics and chemistry of the upper atmosphere, likewise with influences onto Earth's magnetic field due to terrestrial and extraterrestrial events. He created the first (in 1930) model of photochemical dynamics of the ozone layer, which considered the oxygen species O, O₂, O₃, including excited states and hitting partners only. This part of the ozone formation/destruction cycle is still called Chapman chemistry in his honor, all the more recent additions of contributions of hydrogen-, nitrogen-, halogen and other compounds to these processes being just modifications and refinements of this classical model, which itself draw upon Bodenstein's theory of radical chain reactions. Rowland and Molina, primarily trying to understand the chemistry of O and Cl compounds in the stratosphere of Venus (Rowland and Molina, 1974), pointed out the possibly devastating effects of increased organochlorine (CHC, FCHC) and HCl inputs into the stratosphere of Earth and local photochemistry on the ozone layer soon after Chapman's death (in 1974), which earned them the 1995 Nobel for chemistry together with Paul Crutzen.



Sydney Chapman (1888–1970)

It is a classical way of thinking in atmospheric chemistry to consider Earth's atmosphere as a photochemical reactor (see Section 2.2.1), with the troposphere being essentially sealed to the top by the tropopause, to the bottom by the surface of the Earth. Thus, it is closed for rather fast processes like a closed chemical reactor; it takes several months for cross-equator mixing of some compounds specifically introduced on one or the other hemisphere (e.g., the lifetime of CO) whereas fully homogeneous distribution will not be attended unless the compound "survives" at least some five years in the troposphere (e.g., with CH₄, CH₃-CCl₃). Vertical mixing beyond the tropopause into the stratosphere takes even longer although the uneven levels of tropopause (some 8–9 km in Arctic and

Antarctic regions, up to 17 km close to the equator) allow for some “leakage” both of O₃ downward into the upper troposphere (where it is going to cause some problems in using compressed local air inside airplane fuselages and cabins) and vice versa of other compounds into the bottom layers of the stratosphere. Only such organics which are deactivated toward attack by OH radicals or photochemical¹⁰⁾ effects with respect to CH₄ with its five-year lifetime (Atreya, Mahaffy, and Wong, 2007) by corresponding electrophilic substituents (F, CHal₃, CN, NO₂, etc.), that is, FCHC, acetonitrile or nitrocompounds will make their way into the stratosphere from below,¹¹⁾ thereby escaping destruction over decades.

The Chapman chemistry now deals with radical chain processes, as outlined by Bodenstein and Lind (Bodenstein and Lind, 1906; cf. Laidler, 1970), and by this origin puts some emphasis—beyond Chapman’s simple model—on H abstraction and O transfer reactions of halogen compounds. This was first transferred to modeling the atmosphere by Chapman, at about the same time one could start to compare among atmospheres (and their possibly underlying chemistries and photochemistries) owing to the pioneering works on spectroscopy—and thus chemical composition—of planetary (Venus, Mars through Neptune) and satellite (Titan) atmospheres by Wildt (e.g., Wildt, 1932) and Kuiper (Kuiper, 1944). The simplified approach, just considering homogeneous gas-phase chemistry, omitted effects of aerosols, with heterogeneous catalytic chemistry then amply used in technical chemistry but very poorly understood. Accordingly possible effects of aerosols, from catalyzing recombination over interfering with acidic gas phase species [e.g., CaCO₃- or silicate-based particles (Wayne, 1991a), the latter silicates reacting also with hydrogen fluoride (HF)] up to photoelectrochemistry (injection of OH radicals, cleavage of organics by Ti and Fe oxides) were disregarded then, as were the contributions of ion–molecule reactions. For the latter, suggestions to consider

- 10) In the troposphere, admitting UV radiation only beyond (above) some 295 nm wavelength, there will be no photodissociation of either C-F ($\lambda \leq 190$ nm), C-CN- ($\lambda \leq 195$ nm), C-Cl- ($\lambda \leq 230$ nm), C-COOH- ($\lambda \leq 240$ nm, e.g., acetic acid) or C-Br- ($\lambda \leq 280$ nm) bonds; the situation is different with iodo- and to some extent nitrohydrocarbons, ketones and lower aldehydes which readily produce alkyl radicals, H and I atoms, respectively, besides other products like CO, NO₂.
- 11) In the upper stratosphere and mesosphere, there are admixtures of all CH₄, HCN, CH₃CN, HCHO besides water and H₂O₂ and various protonated (Kopp, 1990), acid-solvated and hydrated derivatives thereof, which likely do not come from the surface but are introduced by partial pyrolysis of (carbonaceous) micrometeorites up there. While this apparently is a natural phenomenon,

sometimes enhanced by “near misses” of large meteors/tiny asteroids like the 1965 Grand Teton Mountains (Wyoming) event, noctilucent clouds which are located at some 82 km above ground (i.e., at the level where both unmixing of lighter gases H₂, He, Ne and O atoms from heavier and more familiar N₂, O₂ starts and the local ion concentration begins to increase) were not observed until much after begin of industrial revolution, not even temporally linked to large volcano eruptions.

Accordingly, noctilucent clouds must be considered to give a hint at least that atmospheric pollution did propagate into the upper stratosphere already during the nineteenth century, especially increasing its content of water vapor with correspondingly increased photoproduction of H atoms and OH radicals, contributing to attack on ozone, as does warming of the stratospheric regions.

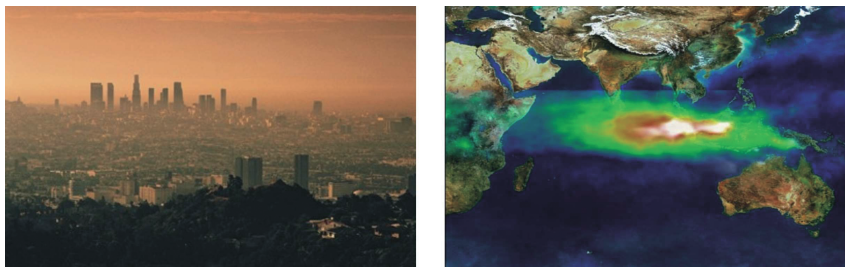


Figure 1.2 Discoloration and increased turbidity of atmosphere due to combustion taking place nearby. Left: Smog in Los Angeles due to car traffic mainly. Right: Slash

and burn agriculture in Indonesia (Borneo) getting out of control, in 1999. Colors encode different levels of smog pollution. Photos: Environmental Protection Agency, July 1999.

them were introduced by cosmochemistry in the early 1970s (about the time of Rowland and Molinas' seminal paper, in 1974), like for the theory of smog formation, concerning both Los Angeles smog (Figure 1.2, left part) produced by photooxidants¹²⁾ including their secondary chemical interactions and London smog, distinguished by formation of polymeric, mainly organic substances (PAHs, soot), likewise. Both technical combustion processes and natural ones, for example, forest wildfires, cause aerosol and smog formation (Figure 1.2, right part).

Generally speaking, feedback analyzes provide quite another concept of causal relations than the classical linear "A causes B, then happens C due to B" and so on since feedback allows for some kind of regulation of the state of a system, permitting compensation for external perturbations or otherwise responding to them (excitability). The branch of science which analyzes structures and feedback pattern/effects in feedback causal system (containing causal loops) is called cybernetics. As a paradigmatic concept, cybernetics arised only about 1950, even though technical devices which involve feedback regulation were invented as early as Greek ancient times, for example, to control water levels (the water closet flush preserves this construction up to today). Later, during the development of power-producing machines, similar devices were introduced by Watt (in 1766) for stabilizing the work rates of such steam engines: a rotating device controls steam inlet rates by shifting a valve position according to centrifugal forces, keeping running speed and power release of a direct-acting (i.e., non-atmospheric) Wattian steam engine constant unless the operator changes the parameters.

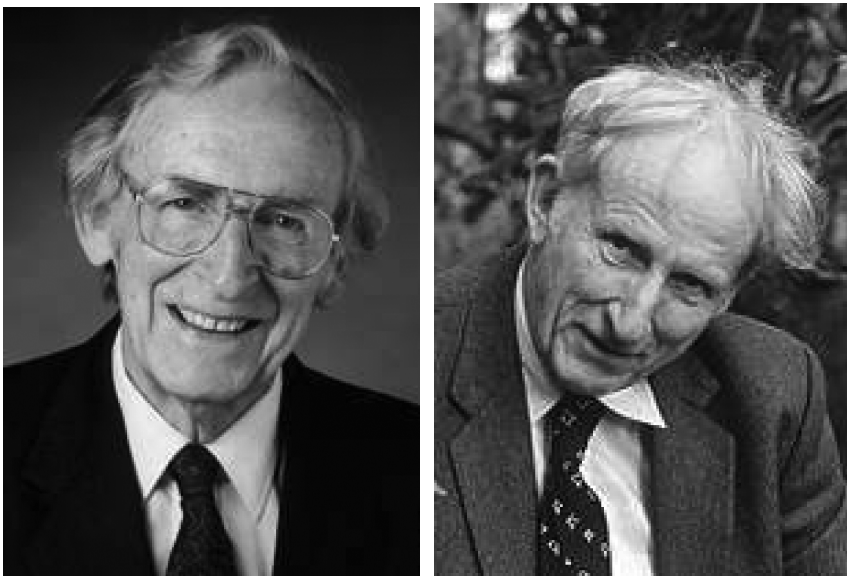
Though the idea of feedback is essential to the entire concept of ecology in biosciences, transport of matter through an ecosystem was considered otherwise, that is, to be mainly linear, for example, speaking of trophic chains rather than trophic nets for long although there is considerable feedback by fungi and bacteria,

12) Note that not all "photooxidants" behave as oxidizing compounds after their formations: while this does apply, for example, to ozone, peroxides like H_2O_2 , or NO_2 , condensates thereof like peroxyacetyl

nitrate, or nitroaromatics present in rainwater, there are other photochemical products, including formic acid $HCOOH$ and aldehydes $RCHO$, which are reductants, rather.

for example. Cybernetic approaches were only later (during the 1960s) introduced into biology, prominently by the Odum brothers.

The principal contribution by the Odum brothers, *Eugene P. Odum*, and *Howard T. Odum*, was to transfer the concepts of energy and matter flow and the ways in which it is controlled in technology including electronics to ecology. H.T. Odum, for example, started his work on what was to become systems ecology with quite classical treatises on an element cycle, namely that of strontium (Odum, 1957), and what it was to tell about larger-scale biogeochemical processes and interactions. Similarly he proceeded to use that horrific extent of radioactive pollution at the United States Eniwetok nuclear test site, with the radionuclides [e.g., ^{90}Sr , ^{65}Zn , rare earth elements (REEs), Pu] also present in the organisms living (or rather surviving) there, for analyzing matter flows in corals and others (Young, 2005). Moreover, they were among the first to use and then popularize the term “ecosystem”,¹³⁾ H.T. Odum additionally introducing the term and concept of ecological engineering (somewhat different from the title of this volume). The enrichment of an element in some volume of matter (be it an organism or something else) being controlled by thermodynamics [a partition coefficient between two phases (one or either of which may be biomass; Fränzle, 2010) is a matter of free-energy differences and thus chemical thermodynamics, solvation or speciation energies] directly led to the notion that energy flows and general thermodynamics were also to shape ecosystems. Their particular emphasis was with the interactions and relations among ecosystems.



Eugene and Howard Odum (1913–2002, 1924–2002)

13) The case whether an ecosystem does actually “exist out there”, rather than be a set of interrelated elements singled out for interpretation purposes by man (scientist) only, may remain open here. It was addressed only much later.

Energy flow in ecosystems and individual organisms and the way it shapes them and their “strategies” is a key concept here, postulating living beings to be optimized in terms of maximum power output rather than utmost efficiency of power generation. Energy and matter storage are accomplished by organisms to survive periods of intermittent energy supply, such as interruption of photosynthesis during night. Analogs from electrical circuit theory, for example, Kirchhoff’s theorem, and from open-system thermodynamics were taken—in a way which remains somewhat controversial—to corroborate the results of the first full-scale measurements of matter and energy flows done by them also (“Silver Spring Study” in Florida, 1972), leading them to postulate additional laws of thermodynamics for purposes of simulating and understanding ecosystems. Thus they made the basis for quantitative understanding of ecosystems operation, including thermodynamic fundamentals governing chemical and photochemical energy conversion, within and beyond the realm of biochemistry.

The shape of the models was suggested by the analogy with electrical circuits, accordingly ecosystems were treated as if containing elements like diodes, switches and energy supplies also.

Now let us turn from discussing individual people to looking into some organizations.

NASA, the National Aeronautics and Space Administration of the United States of America, founded in 1958, in response to the Soviets having launched the first artificial satellites of the Earth before the Americans managed to do so, ever was both a political and a scientific organization (Zimmer, 1996). Anyway, many features now commonplace in their everyday implications for remote sensing as well as communication were introduced by NASA and military satellite applications in the 1960s in the United States, with comparative planetology, enabled by Earth-based astronomy, NASA and Roskosmos alike (Chertok, 2002), providing lots of additional information on both the state of the environment and perspectives to modify and improve it. Polytetrafluoroethylene (PTFE) coatings of frying pans were not due to space research, as common wisdom has it, having been available since the late 1930s, but:

- satellite-based weather forecast, other applications of remote sensing,
- photovoltaics,
- compact high-power fuel cells and
- autonomously operating research vehicles, also of much use in both ocean research and control of highly dangerous man-made environments such as the interior of nuclear powerplants

are indeed due to space research to quite an extent. Thus, though shaped by both instruments (large long-range rockets had been originally constructed for deterrence by nuclear warheads they also could carry) and propaganda purposes of cold war (the race to bring a human to the moon first hardly was motivated by any scientific interest in lunar research, and it produced huge devices no longer of any military “dual use”), NASA and its Soviet counterpart did—and still do, now

augmented by cooperation and others (Europe, China, India, Japan) being also involved—a brilliant though most expensive job in both research pertinent to environmental engineering and in making people aware of the hazards our planet is exposed to by man—and what needs to be done in a hurry; that small blue ball apparently soaring over the lifeless, barren surface of Moon.

Irreversibly changed people's notion of themselves and their surroundings, as later did satellite-derived pictures of, for example, atmospheric (NO_2 maps) or ocean pollution.

1.3

From Environmental Chemistry and Technology to Environmental Engineering: Understanding and Diversifying Anthropogenic Environmental Influences

As outlined before, environmental chemistry deals with understanding chemical processes in the environment while environmental engineering is about tackling present problems in more general ways, also more general concerning the applied methods. Given the extreme but rather frequent case that “pollutants” emitted by nature and man (anthropogenic) are identical, say the parallel emission of solvents chloroform (Gribble, 2005), acetonitrile produced by marine algae and by forest fires, respectively, or that of acid precursors SO_2 and HCl by volcanoes, the “acceptable burden” of environment is just beyond human decision. For example, CO is subject to the same chemical (cleavage by OH radical), photochemical (addition of excited ^3CO to C-H - and O-H bonds) and biochemical processes (oxidation by CO dehydrogenase) whether it originated from volcanoes, engines, coal pits (desorption) or incomplete combustion. Fortunately, while any remediation beyond just saying what happens to CO molecules in the tropos-¹⁴⁾ and biosphere requires knowing where and how much is emitted—and then changing these processes or do end of pipe remediation if feasible, the sources are irrelevant for end of pipe strategies if not directly fitted to the device which emits CO .

This superposition of “natural” and anthropogenic burdens to environment requires to *minimize* inputs as we cannot control the extent of algal growth (except via reducing eutrophication of shallow sea areas) or even that of volcano eruptions. Understanding in environmental chemistry then is understanding the fate of some compound regardless of its origins, concerning all processes, reaction patterns, mechanisms and eventually sinks (and their respective capacities) while remediation obviously must be focused to large-scale or/and high-concentration emission sites and sources. Remediation strategies have to consider specific properties of pollutant sources, like the processes which give rise to some unwanted compound there.

By definition sources release some material, making any structures which act as sources open systems. Technical systems are open ones, too, exchanging both

14) The tropospheric lifetime of CO is about half a year so it will not propagate upward into the stratosphere.

matter and energy with their environments much like living beings do but often at much higher spatiotemporal rates, mainly because temperatures can be attained and used for fulfilling the corresponding task which are beyond biological acceptability. This is why, say, a 100 kW car engine is much smaller (by almost two orders of magnitude) than a whale whose muscles deliver comparable power—and thus similar amounts of CO₂. When, which often happens, other materials are used in technical devices than in biology, materials which are beyond biochemical synthetic capabilities, for example, metals, their production and eventual disposal must be included in any cradle to grave consideration. Then arguments reach far beyond thinking about energy efficiency. In addition, there are less criteria for a technical system not prone to withstand evolution:¹⁵⁾ if plant leaves would not gather much more organic carbon by CO₂ reduction than is required to make them, plants would simply not exist while the total (lifetime) electric energy delivered by photovoltaic cells being in excess of that required to produce high-grade elemental silicon or Si hydrides,¹⁶⁾ gallium chloride or trimethylgallium and AsH₃, SbH₃, respectively, had just to be demonstrated secondarily.

Anyway, an open system is distinguished by exchange with the environment, which has thermodynamic drawbacks (certain equilibrium assumptions do no longer apply) and other consequences:

- energy (often, electric currents such as in electrochemistry) and raw goods or energy carriers/reductants or oxidants¹⁷⁾ must be admitted in a controlled fashion, while waste heat and
- matter products as well as waste products (gases, condensed wastes, ashes, by-products like slag in ore-processing) have to be (steadily) removed from the system or device.

Accordingly, typical devices of environmental engineering are open systems, too. Moreover, they are—at least for end of pipe remediation systems—attached to yet other flowthrough, that is, open systems, for the best purpose of cleaning their

15) Except for effects of market competition, of course.

16) The familiar blue, perceptibly polycrystalline “silicon” solar cells are not made of elemental silicon altogether but rather from hydrogen-containing polysilicon hydrides of approximate composition SiH_{0.15}, prepared by controlled pyrolysis and simultaneous dotation of lower silanes such as Si₂H₆, Si₃H₈ (pyrophoric compounds, by the way) which in turn are made using SiO₂ and elemental aluminium, sodium hydride, H₂ (Riedel, 2004) according to $3 \text{ SiO}_2 + 4 \text{ Al} + 4 \text{ H}_2 \rightarrow \text{Si}_3\text{H}_8\uparrow + 2 \text{ Al}_2\text{O}_3$ (simplified) in a LiCl/NaCl/NaH melt, demanding the energy to produce the above reactive elements (e.g., for Al, >20 kWh/kg).

17) Two common examples: (i) hard coke is used in iron high kilns as a reductant providing the reaction energy to maintain the heat of the system by chemical heating (some 1600 °C, beyond iron melting point, and be it by admission of some air, causing direct C combustion), while (ii) chlorine in organochlorine chemistry acts as both oxidant and reactant by being added in chlorinations of organics like C₂H₄, benzene or CS₂ (even if methods and/or products are outdated now). Here, while elemental C can be obtained from nature (hard coal) with minor modifications, lots of electrical energy is required to obtain elemental Cl₂ from alkali halide brines at all, linking the eventual oxidant/reactant function to prior input of electrical energy.

outputs. In the practical case that an internal combustion engine or fossil fuel powerplant employ air rather than neat oxygen for oxidation of the respective fuels, the combustion chambers will also ingest (very considerable amounts of) N_2 along with O_2 ; in addition some of the fuels (lignite, gasoline) also contain organonitrogen compounds. Combustion (air oxidation) of the latter will afford NO, as will another process: at sufficiently high temperatures (in excess of some 1300°C) N_2 gets thermally excited into a higher electronic state (loosely, N_2^*) which then either emits ultraviolet radiation ($\lambda = 337 \text{ nm}$) or reacts with a variety of chemical species which are present in a combustion chamber, including O_2 (\rightarrow NO), CH_4 (\rightarrow HCN) and so on.¹⁸⁾

Release of NO is obviously due to internal combustion engines being open systems (equilibrium concentrations of NO being extremely low, and what is produced in the heat is “frozen out” by release from the chamber, in case of two- or four-stroke combustion engines this freezing is enhanced by (almost) adiabatic expansion of the gases above the piston, producing cooling rates $\gg 10^5 \text{ K/s}$). Nitrogen is put into the motor in various chemical forms, parts of it to be released as NO_x . In hard-coal powerplants, both contributions from oxidative and thermal NO are comparable in size. Of course, the same consideration holds for all other chemical elements present in either fuel or air provided they are chemically reactive at all (e.g., release of HCl, etc. from salt coals).

If open systems (technically speaking, reaction–diffusion systems) are connected to each other, non-linear behavior may result even if there is no “real” feedback of the second system into the first. The prime consequences are:

- 1) Such throughflow systems never attend “genuine” chemical equilibrium, since chemical equilibrium is (can be) defined for closed systems only. Therefore not only products of doubtful thermodynamic stability are produced during, for example, technical (engine) combustion, adding to the list of potential pollutants afforded there, but in addition one must make sure that (once-again, throughflow, hence open-system) chemical or physical (relying, e.g., on adsorption) transformations meant to remove these pollutants will operate fast enough, that is, while the reaction mixture is still within the device.
- 2) Patterns of uneven reactant concentrations may form, rendering the performance of (too) small heterogeneous catalyst devices essentially unpredictable or prone to temporal oscillations of concentrations of formed intermediates.¹⁹⁾

18) HCN fortunately undergoes further combustion to yield additional NO, while higher hydrocarbons \rightarrow nitriles. Thus nitrogen oxides, NO_2 being produced by NO contacted with (external, cold) air, are formed by both direct oxidation of N-organics (“oxidative NO”, plus those formed involving N_2^*) and thermally induced reaction (“thermal NO”) between the elements nitrogen and oxygen (note that for ground states, equilibrium lies far

to the left, which would cause the highly endothermic NO molecules to decompose almost completely into N_2+O_2 if it were not for this reaction being spin-forbidden).

19) By Onsager’s theorem, oscillations around chemical equilibrium are precluded so the concentrations of the final products do increase steadily. The situation is different with intermediates (De Kepper *et al.*, 1982) including autocatalyst species.

- 3) Such coupling among several throughflow systems may bring about instabilities, chemical oscillations which can jeopardize performance of the cleaning system at all: either the reaction may (apparently) stop for some period of time or occur at such levels (with reactants stored and piled up on interfaces of some heterogeneous catalyst involved) that the device can be overheated and thus destroyed by local excess heat production. All “purely chemical” processes and such which involve biological activity, for example, in sewage treatment devices, are subject to this problem, which, in engines, will be aggravated by rapid and abundant changes in power demand and thus altering gas flow rates. The same holds for sewage treatment plants because inputs vary through the daytime in both amount and composition.

All these problems are related to kinetics: besides demonstrating whether the task of chemical purification can be tackled within the volume of a reactor²⁰⁾ in a given period of time, it must likewise be considered whether the reaction does proceed either in a linear rather than oscillatory manner or at least can be controlled by means of chemical engineering. This does determine not just the size of a required purification device (end of pipe reactor) and whether it can be afforded in all financing aspects, matter requirements (e.g., concerning noble metal components of catalytic converters) and energy inputs, but also whether it will or even can be run in some steady-state mode at all. Hence it will not do to identify methods to either withhold a pollutant from the environment or detoxify it by chemical modification (producing less toxic or hardly soluble secondaries) but there are also issues of kinetics beyond reactor size demands: chemical oscillations are but one possible complication, with chemical waves (reaction–diffusion fronts; Pota and Stedman, 1994) observed in CO oxidation at real-life condition-working three-way converters. After its adsorption, CO is oxidized in a reaction front mode²¹⁾ rather than steadily all over the platinum group metals (PGM)-doped ceramic support. This does not matter for a colloquial converter in a Otto engine car (some 50–100 kW) of some 15–20 cm size since the CO oxidation wavefronts are a few millimeters wide and separated by about 1 cm. However, this would be different when cleaning the exhaust gases of a very small (<50 W output, such devices do actually exist, with some 0.2 cm³ stroke volume) model-propelling four- or two-stroke engine. Figure 1.3 shows both the catalyst and the principal pathways of matter flow in a catalytic converter.

Hence the task to estimate appropriate kinetics and energy balances of a plausible process for a possible environmental protection measure cannot be left to

20) Here, a “reactor” can be, for example, some stage of a sewage treatment plant, the three-way catalytic converter in a car, a photolytic apparatus or even some living being, for example, in phytoremediation, extracting heavy metals from soil by plants growing thereon.

21) This does imply that there must be some autocatalyst formed in CO oxidation at the oxide interface. A reasonable candidate for this would be carbonate ion CO₃²⁻, with

carbonates known to be involved in activation of other heterogeneous catalysts for redox activation of small molecules, like that of N₂ and H₂ in the Haber–Bosch ammonia synthesis. There are many wavefront-forming or even oscillatory processes concerning CH acids in liquid-phase chemistry but only one dealing with CO, namely its formation from formic acid (HCOOH)/sulfuric acid (Morgan reaction [Morgan, 1916]).

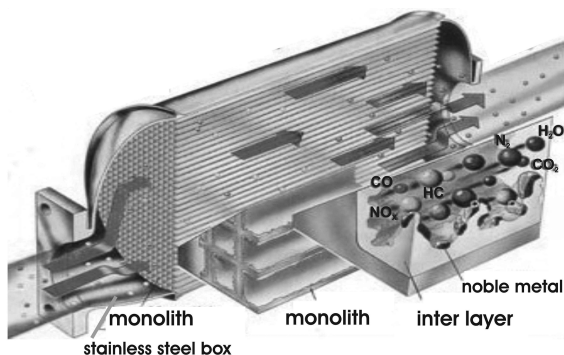


Figure 1.3 A three-way catalytic converter will oxidize both CO and hydrocarbons [all unburned, modified (by thermal partial dehydrogenation, e.g., C₂H₄ or propyne C₃H₄) and secondarily formed ones, like benzene] into CO₂ (and water) while NO_x is reduced into dinitrogen. Here, “monolith” denotes a block of material which is involved in transforming the substrate (exhaust gas), a block rather than a catalyst film covering just the inner surface of a tube. The block need

not be (and actually is not) solid, compact but is porous, with the PGM nanoparticles also covering the inner pores, thus vastly increasing the active surface available for heterogeneous catalysis. The monolith is made from a CeO₂/ZrO₂ (baddeleyite) mixture which absorbs dioxygen (by Ce) and transfers it via platinum group metals to the reducing substrates CO, hydrocarbons (“oxygen spillover”). Photo: Wolfgang Wendt, Berlin.

development engineers but it is more essential: corresponding non-linearities can both preclude up-scaling and down-scaling (like in the fictitious example of fitting a catalytic converter to the silencer of a small or very light model airplane) of a device. Besides, some methods which are successful on a laboratory scale will fail on a larger scale either because corresponding amounts of catalyst components cannot be afforded or because excess heat or by-product expulsion which do not matter on a small scale can no longer be tackled. Once heterogeneities like chemical wavefronts are involved, or retention of process (chemical reaction) heat is required to maintain the system in operation, de-centralized devices for small-scale operations run into trouble, also.

Sometimes, scale-up is precluded just by difficulties of either getting sufficient material or running corresponding larger-scale energy sources.²²⁾ There are examples from all sono-, radio- and photochemistry: although multi-kW sonotrodes are available, their considerable release of low-frequency “waste radiation” (noise, vibrations) renders them awkward to work with—to say the least—while similarly strong radionuclide sources (kW ionizing radiation outputs) are even more difficult to handle for reasons of radiation protection [radioisotope thermoelectric

22) In some cases then substitution is feasible: radioisotope thermoelectric generator (RIG)-sized nuclide radiation sources may be replaced by electron jet sources (Chmielewski *et al.*, 1992; Stiller, 1987)

while the others may be replaced only by some non-coherent light sources (high-power discharge or excimer lamps), if at all.

generators (RIGs), the radiogenic heat production of a lorry-sized Castor container being limited to 40kW] and UV-producing gas lasers (e.g., hydrogen fluoride chemical lasers) for FUV (far ultraviolet; <242nm) or multiphoton photolysis become very large also. Sometimes parameters to run a device can be altered so much as to avoid non-linear behavior. For simple cases—including CO oxidation—limiting conditions for chemical wavefronts or/and (e.g., the Belousov/Zhabotinsky system) oscillations can be determined from theory (e.g., Eiswirth, Freund, and Ross 1991a,b; Eiswirth *et al.*, 1996) but this powerful and efficient method (stoichiometric network analysis) is beyond the scope of this work and also has met but limited practical applications. The more straightforward way to see what happens by changing device dimensions is to link laboratory scale to large-scale apparatus by running a semi-technical scale apparatus.

While environmental chemistry is just concerned with what might be done or with an understanding of natural processes, considering the above dynamic, kinetic and correspondingly technical criteria is required to turn this into “real” technical environmental chemistry or, more generally speaking, environmental technology. Ways to do this and ramifications are discussed near the end of this book, dealing with case studies (Chapter 4).

Apart from this, one must understand the underlying individual processes and their fundamentals, for example, those ruling reaction kinetics at aromatic compounds (Hammett equation; see Section 3.2.3) or redox reactions (redox potential relationships—superposition of Pourbaix diagrams; see Section 3.2.2, Marcus equation) obviously required even to conceive any plausible process, regardless whether it can be scaled up to technical applications at all. All processes are limited with respect to expendable matter and energy flows. The other criterion is borrowed from medicine: Like the oath of Hippocrates demands the doctor not to put additional harm/damage to the patient by his treatment methods (*nihil nocere*), all these processes (the details of which are often poorly understood) must not bring about additional environmental problems. Cases which violate this criterion or principle would, for example, include the production and release of toxic secondaries from some process or the enhanced dispersion of either the original pollutant²³⁾ or some secondary thereof.

How is environmental technology done, then? Now, first of all, environmental methods can either be a reapplication of such procedures which are already established—like in soil remediation where all the strategies of modern mining of low-grade ores or even waste materials are employed in very much the same manner—or the technical solution may be/have been developed for the purpose of cleaning or

23) During the application of chelators (multidentate complex-forming anionic or neutral ligands) to topsoils both for direct extraction of heavy metals and for better performance of phytoremediation measures (plants [and fungi] also make use of chelators such as malic, citric or oxalic acids, certain amino acids, or hydroxamic acids, these moieties

sometimes combined in a single molecule) there also are unwanted kinds or aspects of mobilization: nutrient (cations) may be leached or no longer be bioavailable, pollutants such as Pb, Cd, (excess) Cu, or Be may be mobilized without being completely removed by the plant grown for extraction simply because its rhizosphere is spatially limited.

protecting the environment specifically. Often just some parameters of a given technology or catalyst were adjusted:

- European-style catalytic converters use the very platinum group metals (PGM) alloy of Pt/Rh 5:1 for NO_x removal which was established long before (Ostwald's catalyst) for air oxidation of NH₃ to nitrogen oxide in nitric acid production.
- Hydrogenation splitting of old tyres or plastic wastes into liquid hydrocarbons is done using the same catalytic interfaces as the Fischer–Tropsch hydrogenation of either lignite or hard coal was done for decades at Leuna in Germany (then the German Democratic Republic; GDR) and South Africa, moreover at similar H₂ pressures, temperatures and catalyst compositions.

This alternative just deals with the level of the practical technical approach but not the principal strategy as not a single approach, including techniques from and using biochemistry, is known which was originally designed to improve protection or status of the environment (Fränzle and Fränzle, 2002). For example, fuel cells were a chance discovery, and the arduous attempts by Ostwald and others to use/"burn" coal in high-temperature cells did not deal with environmental protection but with reducing the steps of energy conversion until eventually an electric current is obtained [in addition, these attempts to replace hydrogen or methanol (which must first be prepared) with coal in fuel cell devices were futile]. The case is similar to the direct photocleaning of water [by photocleaning by extreme ultraviolet (EUV), or vacuum ultraviolet (VUV; <200 nm)], removing dissolved xenobiotics at $\lambda \leq 200 \text{ nm}^{24)}$ or photoinduced hydrolysis of halogenated aromatics. The main reason for this would be that technical environmental chemistry and general environmental engineering are far younger issues than the onset of basic research in chemistry, photochemistry and technical physics which in large parts—except for semiconductor and nuclear techniques—can be traced back almost to the very industrial revolution which aggravated those problems later on to be tackled by environmental engineering.

1.3.1

Meaning of Pollutant Degradation

One can alter, modify or degrade chemical compounds considerably but only up (or rather, down) to some well-defined limit. This limit is set by the level of chemical elements, which were defined already long before nuclear techniques were even conceived of, along the following—empirical—rule, dating back to Lavoisier (1780s):

Chemical elements (fundamental radicals, as Lavoisier called them) are “substances which cannot be separated any further by chemical means.”

24) Andre Braun and co-workers, Engler-Bunte Institute, Karlsruhe, Germany, personal communication.

Obviously, this definition does not completely conform to present (after about 1920) knowledge: some electrons can be removed, often rather easily, from a metal atom to produce cations which then are stable in lowly nucleophilic media whereas kinetic isotope effects in chemistry cause some separation (an almost complete one in the hydrogen/deuterium case) among the isotopes of some element during chemical transformation (Preetz, 1969; Krumbiegel, 1986); when, for example, chlorate ClO_3^- is reacted with hydrochloric acid (both isotopically “normal”), the produced (elemental!) chlorine will contain more $^{35}\text{Cl}_2$ rather than ^{35}Cl , ^{37}Cl and $^{37}\text{Cl}_2$ than corresponds to the colloquial 75.4% ^{35}Cl ; 24.6% ^{37}Cl mixture, that is, more than some 57%. Thus some additional separation within an element took place. However, the above definition, although more than 200 years old now, remains to be valid in a way which is most relevant to problems of environmental engineering: regardless of kinds or numbers of chemical or biochemical transformations exerted to the given substance, the atoms of which it is constituted will never “vanish”. It is just possible to bring them into some different chemical bond network, including the elemental state (N_2 , Hg, etc.). This statement holds for all chemical elements, and there is almost no influence of chemical environments on radioactive decay either; and it holds for metals and non-metals alike.

What then is the meaning of the familiar assertion that organic substances, that is, carbon compounds other than carbonates, cyanides, CO, CO_2 or urea, “can be degraded” in either chemical or biological processes whereas heavy metals or their salt complexes cannot? While C or N atoms are as indestructable by chemical means as those of Cd or Ni, we shall soon see that non-metals respond to changes of chemical speciation, be it those of oxidation state, complexation or within covalent structures, with far more pronounced changes of toxicity than are observed in metal compounds or complexes. Toxicological data are often determined with rats (*Rattus norvegicus*), with the toxins being applied in various ways (LD_{50} doses; here: oral). Thus, among F-, Cl-, P- or N compounds toxicity data for simple alkali metal salts of these elements (fluorides, chlorides, phosphates or nitrates, respectively) are compared to action doses of such organic poisons bearing the same elements in a way in which the toxic action can be attributed to the non-metal heteroelement by comparison with closely related compounds lacking this element. The four highly toxic counterparts for F, Cl, N and P, respectively, are: (i) monofluoroacetic acid, which blocks the Krebs cycle mimicking the citrate ion (F), (ii) the notorious dioxin 2,3,7,8-TCDD (Cl), (iii) tetrodotoxin (N), the action of which against the sodium ion channel in nerve cell membranes is caused by the protonated carbamidine function²⁵⁾ (three N atoms) and (iv) the chemical warfare agent soman (GD, the German CW agent D, the isohexyl-2-ester of methylphosphonate fluoride; P; Figure 1.4). While other, more complicated carbamidines such as saxitoxin can be similarly toxic [human lethal dose 1–2 mg (!)] as tetrodotoxin, specific blocking of Na^+ channels is the toxic principle as carbamidines otherwise can very well be dealt with by metabolism; cf. the essential amino acid arginine and its role as a transamination agent in urea biosynthesis (ornithine/

25) To the left in the picture of tetrodotoxin (Figure 1.4).

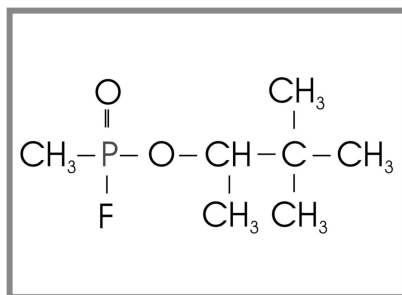
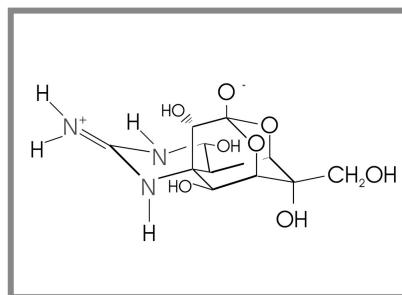
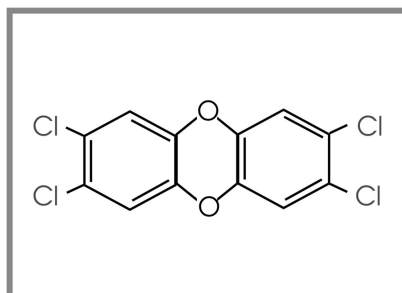
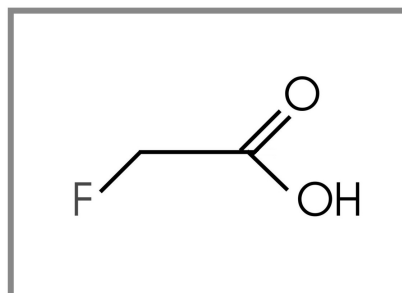
*Soman**Tetrodotoxin**TCDD**Monofluoroacetic acid*

Figure 1.4 Highly toxic speciation forms of four different non-metals F, Cl, N and P. Pnictogen compounds: soman (GD) and tetrodotoxin. Halogen compounds: TCDD and monofluoroacetic acid.

arginine cycle). Soman and similar phosphonates will phosphorylate serine residues in enzyme acetylcholine esterase much as simple polyphosphates do but in an almost irreversible manner, with a pile-up of acetylcholin in the synaptic area jeopardizing nerve functions once again. These four compounds are found to be relatively much more toxic when compared to the above alkali salts than are different binding/speciation forms of say, mercury or chromium. Allowing for biomethylation or technical applications of arylated or alkylated, hydrolytically stable organometal compounds, the range of toxicities to be covered by different speciation of a given metal or semi-metal (e.g., Bi) might become almost as large as with non-metals, for example, tetraethyltin²⁶⁾ is about 20 000 times as toxic toward rats than SnO₂. Accordingly for metals desalkylation becomes a task in

26) Although it is known as a low-melting metal under ambient conditions, tin does chemically resemble its lower congeners Si and Ge far more than it compares to Pb given, for example, the stability and chemical properties of hydrides (SnH₄, Sn₂H₆), compounds which contain E-E

bonds, oxoanions and so on. Its metal character (>286 K) is limited to the relative vicinity of its 505 K melting point, again like with silicon and germanium, with Sn becoming a small band gap semiconductor below 286 K also, thereby crumbling into covalent crystals ("tin pest").

technical detoxification; usually it is facile to achieve but sometimes matters are different: while tri- or tetraorganotin can be stripped of their alkyl groups by electrochemistry (Stichnothe *et al.*, 2005) readily, the $(\text{CH}_3)_2\text{Tl}^+$ cation will withstand prolonged cooking in 68% nitric acid (Elschenbroich and Salzer, 1988)! In fact, apart from its (likewise enhanced) toxicity (while that of Tl^+ alone is more than considerable) is so stable against oxidation and photolysis that, given the ability of bacteria and fungi to biomethylate Tl (Thayer, 1995), it is difficult to see why there are any speciation forms of thallium other than $(\text{CH}_3)_2\text{Tl}^+$ cation in seawater—and even prevail (Schedlbauer and Heumann, 2000). After all, “heavy metals and their compounds cannot be degraded” really means that “speciation does not matter so much with respect to toxicity than with non-metals (pertinent speciation forms of the latter being almost always covalent and often organic compounds).” In addition, the effects of oxidation states are *inverted*.

In heavy (and some light, e.g., Eu, V) metals higher oxidation states are more toxic (e.g., chromate, Cr^{3+}) than lower ones because oxidized complexes tend to be more stable and thus metals bind more strongly to amino acid side chains and other kinds of biological matter, causing havoc in enzymes whether or not these need metals to operate. In non-metals the situation is different: here reduction means creation of vacant electron pairs at the non-metal site which then readily coordinate to (especially “soft”) metal centers in biomass, which is the mode of action for toxins like CO, CN^- [C(II)], triorganotin *anions* [Sn(II), inorganic As(III)] or trialkylarsines, -stibines, PF_3 . Once the propensity for specific ligand behavior is removed, toxicity does vastly decrease, for example, tertiary arsine oxides (among them many biogenic ones), $\text{As}(\text{CH}_3)_4^+$ and arsenobetaine (also biogenic) are far less toxic than trimethylarsine or similar compounds, NCO^- less than CN^- and so on.

Similar compounds which bear different halogene and pnictogen atoms ($\text{pn} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}$, element 115), like bromoacetic acid, brominated or iodinated dioxins or arsonate esters, are far (by several orders of magnitude) less toxic than the four compounds mentioned and depicted above, and the same holds for substances with a differing number of halogen atoms (di-, tri-, heptachlorodibenzodioxins, difluoroacetic acid, etc.). Such organic halogen compounds (or other electrophilic, alkylating agents like oxirans, aziridines, esters of strong acids like dimethylsulfate), including chloroform CHCl_3 or the above fluoroacetic acid, can add to organic compounds and thus influence biochemistry²⁷⁾ far more than coordination of respective anions to metal centers would do. Soman or TCDD (there are similarly toxic compounds including the heavier halogens, e.g., among bromination products of dimeric cyclopentadiene) are just extreme cases of this effect. However

27) Organic electrophilic agents, like chloroform and ethanol (via formation of ethyl esters, chloroethane in stomach or ethanal CH_3CHO ?) or oxiranes, thus also induce metallothionein (MT) formation by addition to the recognizing sequence of

nucleic acids which then unleashes MT- gene expression. It does not really matter here whether a metal ion does add to this particular strand by coordination or an organic electrophile alkylates it.

also certain non-metals, whether these are susceptible to biological reduction, cannot be “thoroughly detoxified” by appropriate speciation, like boron and sulfur.

These chemical options (principal, among others) can be used for reducing the toxicities and/or solubilities of compounds of different elements:

- A redox process can be used to detoxify some element: Cr(III) is both less toxic and less bioavailable than chromate(VI), which in addition is carcinogenic, whereas As(III) is far more toxic than arsenate(V).²⁸⁾
- Precipitations of sulfides or hydroxides/aquoxydes reduce bioavailability to an acceptable extent, allowing the later deposition or other use of the substances (e.g., production of glass, concrete from phosphate precipitates, fly ash, respectively).

While there are various methods to detoxify organic substances by dehalogenation, just a few of them can be applied similarly for the removal of heavy metal wastes (if similar or identical conditions apply for different classes of compounds, fewer steps are required for comprehensive detoxification). However, heavy metals which are rather toxic, at least in some speciation forms, can often be precipitated as pure metals under conditions which otherwise bring about the dehalogenation of organics, that is, the addition of reductants. The majority of heavy metals are distinguished by not-too-low redox potentials [except for rare earth elements (REEs), actinoids]. Conversely, transfer into the elemental state is a viable option for a few non-metals (nitrogen, sulfur, arsenic); but it vastly increases the toxicities of others (halogens). Among attempts for the oxidative²⁹⁾ “destruction” of (mainly organic) pollutants, two principal (yet, sometimes, consecutive) outcomes must be distinguished:

- 1) Degradation of the primary compound, that is, conversion into other compounds containing still element C bonds which are (usually) still oxidizable further—even though this might take drastic conditions, given that, for example, the oxidation of sulfur organics by $\text{HNO}_3/\text{H}_2\text{O}_2$ under pressure and microwave heating does end up at methansulfonate $\text{CH}_3\text{-SO}_3^-$ rather than proceeding into sulfate (Krümmel, 1988).
- 2) Mineralization which converts C and H species entirely to CO_2 and water while other elements (N, halogens) can remain in and be released in some

28) Back in sixteenth century, Paracelsus discussed the already then established method of “improving” the outer appearance of horses going to be sold by feeding them some As compounds. He stated (data given in modern terms/units) that “some 3 g of white arsenic (i.e., As_2O_3) are capable to kill a horse” while “even about 100 g of As compounds (modern terminology) are tolerated if fired with potash in air before giving it to the horse”

(the $\text{K}_2\text{CO}_3/\text{O}_2$ system producing K arsenate[V] K_3AsO_4). Either dose is remarkably high with respect to humans and the man/horse weight ratio.

29) In reductions there is no comparable process, since the C backbones are conserved even though O and halogens (Hal) are cleaved as water and Hal^- , respectively. Some nitrogen compounds, like nitrocompounds, can thus even be increased in toxicity.

reduced form (Cl^- , NH_3) even after the application of drastic oxidation means, like advanced oxidation procedures (AOP).

Often the “efficiencies” of degradation methods are discussed without distinguishing between mineralization and some–limited–restructuring of the primary substance, without even considering toxicological implications of the latter.³⁰⁾ It is commonplace to distinguish between decomposition [$x.y\%$ of the original substance have “vanished”, total organic carbon (TOC) is decreased by some amount during treatment] on one hand and by chemical or biological oxygen demands on the other. While the former parameter refers to just a single substance, perhaps one component of a complex pollutant mixture, which is removed to a measurable extent while this afforded products of unknown, possibly larger ecological hazards, with oxygen demands for mineralization essentially unchanged. If atmospheric oxygen—as the terminal electron sink—or at least NO_3^- is not available or just to a very limited extent (lower soil or water layers³¹⁾ this difference between degradation and mineralization becomes the more pronounced although some organisms can mineralize organics almost completely on Fe^{3+} as an oxidant.

Both biological/biochemical processes and others in atmospheric photochemistry—involving far ultraviolet (FUV, $<242\text{ nm}$), OH and NO_2 , NO_3 radicals—are likewise capable to convert rather harmless compounds like ethyl fluoride, 1,1,1-trichloroethane (methyl chloroform) or naphthalene into more toxic ones [here, monofluoroacetic acid, the plant poison trichloroacetic acid, increasing deserted areas in Central Asia, and nitro or nitratonaphthalenes and -naphthols (Pitts *et al.*, 1978; Schauer, Niessner, and Pöschl, 2004, respectively)]. Locusts, mussels and even vertebrates (fishes, frogs) take up and eventually chemically modify xenobiotics, biocides or the products of marine algae and bacterial metabolisms to the extent that they can employ these compounds as poisons against predatory organisms. Here, evolution takes place on time-scales of just decades. Similar effects may also occur in those both poorly defined and highly dynamic consortia of microorganisms which do the job in biological sewage treatment plants.

To give an example, Table 1.2 shows the size of toxicity differences (rather, ratios) for the different speciation forms of 13 elements. This includes

30) Cf. the results of NUV (near ultraviolet ($\lambda = 325\text{--}380\text{ nm}$))/ O_2 photooxidations of polycyclic aromatic hydrocarbons (PAHs), yielding quinones or the photohydrolysis of chloro- or bromoarenes which produce phenols, both being more toxic than the original compounds. Polycyclic quinones formed in the self-sensitized (triplet PAH) O_2 photooxidation of PAHs are bactericidal compounds (obviously detrimental to environmental further degradation) and, besides, toxic (oxidative decoupling) and carcinogenic to metazoans (Brack *et al.*, 2003; Bataineh *et al.*, 2010).

31) If pollutants which can be almost exclusively oxidized by dioxygen are buried in soil and it is undertaken to oxidize them there by pumping air down into deep soil layers by injecting compressed air or H_2O_2 solutions, the oxidation of both sulfide and Fe(II) will onset. One result is a decrease of pH (soil acidification), with several heavy metals put into soluble and mobile states. A deliberate form of this process is bacterial leaching of metals like tin, copper or uranium (cf. Section 4.2.1 on soil remediation methods).

Table 1.2 Toxicity against rats (LD₅₀ oral) for the same element in various binding states.

Element	Class	Weakly toxic	LD ₅₀ (mg/kg)	(mMol/kg)	Strongly toxic	(mg/kg)	(μMol/kg)	Quotient
V	L	VCl ₃	350	2.25	NaVO ₃	98	0.80	2.8
Fe	H	Fe(III) nitrate	3.250	8.0	Fe(II)SO ₄	319	2.100	3.8
Hg	H	Hg ₂ Cl ₂	210	0.9 (Hg)	Hg(NO ₃) ₂	26	80	11
B	N	Na ₂ B ₄ O ₇	2.660	28 (B)	NaBH ₄	69	1.800	16
S	N	K ₂ SO ₄	6.600	38	Thioglycolic acid	73	800	47.5
Cr	H	Cr(III) nitrate	3.250	8.1	K ₂ Cr ₂ O ₇	25	170 (Cr)	48
As	S	Arsenocholine ^{a)}	6.500	39	As ₂ O ₃	10	100 (As)	390
F	N	KF	245	4.2	Na(F-CH ₂ CO ₂)	0.2	2.2	1900
P	N	Na ₂ HPO ₄	12.930	48	Soman	0.4	2.4	12 000
Sn	H	SnO ₂	>20.000	>130	Tetraethyl tin	16	70	>18500
N	N	NaNO ₃	1.267	15	Tetrodotoxin	0.005	0.04	375 000
Cl	N	NaCl	3.000	51	TCDD	0.001	0.0125 (Cl)	4*10 ⁶

a) Trimethylarsonioethanol cation; [(CH₃)₃As-C₂H₄OH]⁺ gets oxidized to arsenobetaine in the human body also, being highly hydrophilic and subject to renal excretion. For some compounds listed here, for example, dermal or intravenously toxicities are even considerably higher. H = heavy metal, L = light metal, S = semi-metal, N = non-metal. The factor (quotient) given in column 9 relates the toxicity of a given highly poisonous speciation form (column 6) to that of a lowly toxic one (column 3).

organoelement compounds which represent the minimum of toxicity for As³²) while it corresponds to the respective toxicity maxima against rats for Sn, P and Cl. Concerning Fe, Hg (!), Cr and several other elements, organoelement compounds form neither extreme but are intermediate with respect to rat toxicities.

In non-metals, especially their rather complicated compounds like tetrodotoxin (Figure 1.4), attributing the “toxic principle” to a given element (column 1 of Table 1.2) might appear somewhat arbitrary, prompting the following remarks:

- Dioxin toxicity mainly depends on chlorine content and the halogen substitution patterns of the corresponding isomer, making 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD, Figure 1.4) a chlorine compound in its toxic mode of action.
- Fluoroacetic acid (Figure 1.4) and its Na salt, or -esters are more toxic than the other monohaloacetic acids and even than cyanoacetic acid by orders of magnitude.
- In “design” (Schrader’s formula) or nerve chemical warfare (CW) agents, phosphorus may not be replaced by other central atoms producing oxoanions and esters readily (S, As, Cr, etc.).
- Tetrodotoxin,³³ rather than a protein “ultrapoison” like botulinus toxin, is regarded as a specific nitrogen compound because the carbamidinium ion moiety [not the strange arrangement interlinking an octose (!) sugar to a carbonate ester site] is (out-)competing Na⁺ in the sodium channels of some nerve.

Which organisms actually produce tetrodotoxines (all algae, dinoflagellates and marine bacteria are presumed to do so) is still a matter of debate. Anyway, it is accumulated in the livers of bellyfish (*Tetrodo*), in the skins of certain *Dendrobates* and *Phylllobates* poison frogs (which dwell far from any ocean in Central and Southern America!), in some mussels and other mollusks (different parts of the small blue-ring octopus *Atelopos zelecki*) and is used there for either defense or making prey (in the squid mentioned before). Either technical or biological alkylation is capable of altering the toxicities of elements in either direction (though increased toxicity is more common). Exposition of mixtures containing elements

32) As noted before, there is a difference between non-complexing quaternary arsonium salts like arsenocholine (trimethylarsonio)ethanol or As(CH₃)₄⁺ and ternary ones which still act as ligands: “lewisite” CH(Cl)=CH-AsCl₂ is that toxic and irritating, breath-impairing (causing people to tear off their gas masks) that it was abused as a chemical warfare (CW) agent during WW1. Concerning rats, its toxicity is similar to that of As₂O₃. The principal difference is that arsonium salts are rather inert (though possibly lipophilic

in cases like AsPh₄⁺) whereas the three-coordinate As compounds act as ligands, much like CN⁻, CO, PF₃, blocking Fe binding positions while lewisite and similar compounds in addition will react with cystein residues of proteins.

33) Distribution of tetrodotoxin in the 38 different species of bellyfish eaten in Eastern Asia differs strongly, requiring corresponding taxonomical expertise of the cooks who prepare these fish for the frying pan or sushi . . .

which are sensitive to ambient conditions (e.g., reducing media, rich in organics capable of transmitting methyl groups) often allow for biomethylation³⁴⁾ of both metals and non-metals. This can thus either increase or decrease the toxic risks of the above mixture [Challenger's or Feldmann's experimental setups (Challenger, 1945; Feldmann and Cullen, 1997)]. The same holds for oxidating conditions, depending on the presence of certain elements. Hence, analysis of the composition of, for example, a superfund site is essential before doing any change to the internal conditions. Oxidized forms are more toxic in V, Hg, and Cr, less so in Fe and As. Relative toxicity changes increase in the order: vanadium (III; V) < iron (II; III) < mercury (I; II) < chromium (III; IV). The toxicity of a metal-organic compound, chromium hexacarbonyl, $\text{Cr}(\text{CO})_6$, [$\text{Cr}(0)$, $\text{LD}_{50} = 1.05 \text{ mmol} = 230 \text{ mg/kg rat}$] lies between the toxicities of soluble $\text{Cr}(\text{III})$ and chromate.

For carbon or chlorine compounds, it is possible to alter toxicity values by changing the binding networks to an outright dramatic extent by, respectively, up to six or 11 orders of magnitude. For "heavy metals",³⁵⁾ this possibility is much less pronounced. The term "heavy metals" (introduced back in 1904) to denote certain toxicological—rather than just chemical—features now is mainly considered outdated for reasons of indeterminate, if not arbitrary use; many even recommend to omit it altogether. However, for example, Fränzle and Fränzle (2002) identified those common features in terms of quantum chemistry which cause "softness", thiophilic behavior, pronounced tendencies for complex formation and also high toxicity of so-called heavy metals all alike. Among these, chromates(VI) and trivalent Cr salts differ by some factor of 50 (1.7 orders of magnitude), only, for other metals the differences among toxicities of speciation forms are even smaller. The larger effects for Hg and Cr are not related to the formation of covalent compounds like CrO_4^{2-} oxoanion or the Hg_2^{2+} clusters chemically differing from rather ionic

- 34) Introduction of other alkyl or even aryl groups than CH_3 , including ones which bear additional functional groups (-OH in arsenocholin, arsenosugars, -COOH in arsenolipids) is apparently limited to As and Hg, while binary hydrides (rather than alkyls) are formed by biology with even less elements than methyls are (not with Se, Te, Sb, Bi, Ge), plus PH_3 . Hence, it is justified to call the process simply biomethylation and estimate the effect of binary alkyls (the neutral polymethyl ones not being formed with elements such as Tl, Sn, Pb, Au or Pt) using data on methyl compound toxicities.
- 35) A simple comparison of chemical properties along groups of the periodic system of elements (PSE) actually reveals that chemical features of "light metals"—sulfides undergoing ready, if not vigorous, hydrolysis rather than being precipitated from aqueous solutions (Al,

Ga vs In), violent reactions of metal alkyls with both air and water rather than their formation by biomethylation in aqueous media (Al vs Tl)—can be related to one limiting value of metal density, which is 6.0 g/cm^3 . The heavy alkaline earths Ba and Ra (which are below this limit) behave much like their lighter congeners Ca and Sr, while V differs considerably from Nb and Ta; and Eu ($\rho_{\text{metal}} = 5.26 \text{ g/cm}^3$) differs considerably from all the other rare earth elements (REE), as do Sc, Y from La, REE (except Eu) and Ac. Considering the fact that quite often much lower "threshold densities" are introduced in an obviously quite arbitrary way (5.0 or even 4.5 g/cm^3), without actually considering the above facts quite well-known to both inorganic, bio-inorganic chemists and toxicologists, the term should no longer be used unless giving a working definition like this before.

species: Hg(II) compounds like HgCl_2 are not ionic either—used as non-electrolytes in aqueous or similar donor solutions (Waddington, 1972; Cotton and Wilkinson, 1981)—and Cr(III) forms complexes readily which are kinetically fairly inert although not very stable in absolute thermodynamic terms. Remarkably, fluoro-complexes—including those which will not undergo hydrolysis *in vivo*³⁶—are considerably more toxic than both other speciation forms of the same element or fluorides of Na, K.

Reconsidering heavy metals, effects are superposed which include:

- Substitution/removal of physiologically present and active metal ions from proteins, where they are labily bound (see Fränzle 2010 for the reasons of this)—for example, of Zn by Cd or of Fe by group 13 metals Ga or In, often causing
- Blockade of active centers, which also occurs when thiolate groups react with heavy metals M^{2+} (e.g., $\text{M} = \text{Cd}, \text{Hg}, \text{or Pb}$), alcohols or phenols, serine, threonin or tyrosine residues react with Ti(IV), precluding their functional control (“switching on or off”) by phosphorylation, eventually
- Differences in resorption efficiency and sites of possible accumulation owing to unlike speciation: along the sulfate carrier, chromate gets transported all the way into cellular nuclei where it oxidizes nucleic acids (Wetterhahn and Hamilton, 1989), amino acids and sugars, being retained as Cr(III) then, while just a few percent of original Cr(III)³⁷ become resorbed (Figure 1.5, modified after Kaim and Schwederski, 1991).

In environmental technology, the treatment of xenobiotic compounds is considered successful when some combination of the following effects is achieved:

- Acute (short-term) detoxification;
- For organic and element-organic target materials, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) values approach zero after

36) At least as far as can be guessed by lack of fluoride necrosis in tissues. Human serum, for example, is highly aggressive toward covalent fluorocompounds, readily destroying polytetrafluoroethylene (PTFE) interfaces (hence, PTFE cannot be used to cover the interfaces of artificial joints in humans or other mammals) and rendering fluoroacetate, S_2F_{10} , extremely toxic. Possibly this also holds for fluorocomplexes of metals like Al, Fe and rare earth elements. A notable exception among fluorocarbon compounds or functional groups is the CF_3 group which can be produced by some unidentified marine organisms apparently (presence of substantial CF_3COO^- in parts of the deep ocean not accessed by CFHC downmixing yet; Frank *et al.*, 2002). CF_3 functions as

such are no subject to biodegradation (cf. fluoroorganics like halothan, perfluorated tributylamine, R134a, or R113) or to electro- or nucleophilic attack.

Correspondingly trifluoromethyl groups are often introduced in pharmaceuticals for enhanced stability, such as with fluoxetine (Prozac™), which is a β -phenethylamine antidepressant agent with a para-trifluorotolyl ($4\text{-CF}_3\text{-C}_6\text{H}_4\text{-}$) group.

37) Among the metals mentioned here, Cd was proven essential and involved in enzyme function of certain algae (*Thalassiosira* spp. [Strasdeit, 2001]), with mammal (goat) essentiality also likely at least (Anke, Groppe and Schmidt, 1987; Memiši *et al.*, 2008), while essentiality of Cr for animals including man is now considered unlikely (Stearns, 2000).

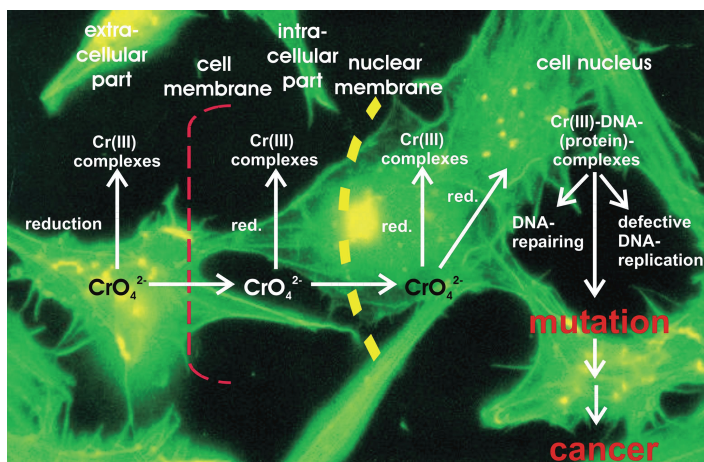


Figure 1.5 A schematic representation of uptake and reduction of chromate, linked to its mutagenic activity inside cells (courtesy of underlying photograph: Prof. Barnekow, Department of Experimental Tumor Biology, Münster, Germany; scheme overlaid by the authors).

treatment, excluding uncontrolled remobilization or retoxification of materials in either aerobic and anaerobic conditions, more generally speaking;

- Production of speciation forms which are “green” or compatible with environment for long periods of time (non-toxic, inert, insoluble or at least incapable of harming environment by subsequent reactions which produce secondaries relevant to, e.g., climate change or atmospheric chemistry).

With phosphorus, tin, fluorine or chlorine—other than arsenic—a comparison among toxicities of “organic” and inorganic (mainly, salt anion) binding/speciation forms of these elements shows that destruction of element-carbon (E-C) bonds will cause considerable decreases of toxicity: phosphate or phosphonate esters, including both “agrarian” biocides and chemical warfare (nerve) agents, fluoroacetic acid, polychlorinated dioxins, -dibenzofuranes and di-, tri- or tetraorganotin compounds are so much more toxic than inorganic halides or phosphates or SnO_2 , that it really does not matter how mineralization (i.e., complete degradation of E-C bonds) is achieved. Some practical options for the above purposes include:

- Reductive dehalogenation;
- Electrochemical oxidation (Sn and Pb organyls, halophenols), including catalysts like $\text{Ag}^{+/2+}$ (dissolved, P-based CW agent cleavage);
- Hydrolysis of haloaromatics using UV radiation, producing corresponding phenols;
- Cleavage of organohalogens in conditions of silent-discharge oxidation (combustion by OH radicals or electrochemical reduction; Kopinke *et al.*, 2000);

- Photoelectrochemistry (oxidative and reductive processes at the same, photoexcited semiconductor; Fränzle, 1996; Kokorakis *et al.*, 2000; Fränzle *et al.*, 2010) in a system which consists of a colored oxidizing metal complex adsorbed to a broad-gap semiconductor;
- High-temperature hydrolysis and oxidation (“fluid combustion”) in supercritical water vapor.

These methods are discussed in more detail later, so here it suffices just to describe the basics:

- 1) Halide ions can be removed from C-Hal (\neq C-F-) bonds readily by electrochemical means (cathodic reduction), solvated electrons in liquid NH_3 , amines or by heating with appropriate reductants like solid/molten sodium oxalate.
- 2) Organotins may be oxidized to SnO_2 hydrate and the corresponding alcohols at an anode (Stichnothe *et al.*, 2005). Catalytic varieties (Weinberg and Weinberg, 1968; Kyriacou, 1994) include anodic formation of reagents like Ag^{2+} , $\text{Co}^{3+}_{\text{aq}}$, Ir(V) —attached to the interface—which, although short-lived in water themselves,³⁸⁾ react so much faster with the corresponding pollutants, including phosphonic chemical warfare (CW) agents in the silver system (Emsley, 2001), that the latter can be cleaved, abstracting halogens other than F in the same turn.
- 3) Aromatic and some aliphatic organohalogens undergo *hydrolysis when exposed to UV radiation* in aqueous solution or suspension. This even is used in UV dosimetry, with quantum yield $\Phi \approx 1$ for chloride formation from ClCH_2CO_2 ⁻³⁹⁾ at $\lambda = 254 \text{ nm}$ (Becker *et al.*, 1991) whereas chloro- or bromobenzenes form phenols and Hal^- ions. Nitrocompounds can undergo both nitrite cleavage (in the same manner) or intramolecular photooxidations. Haloarene photohydrolysis, however is a critical feature especially when it occurs with $\lambda \geq 300 \text{ nm}$ in halo-PAHs: while glycolate is much less toxic than chloroacetate, quite the opposite holds for chlorinated or brominated benzenes and toluenes: in the rat (oral application), ortho-methylphenol (2-cresol) is about 40 times more toxic than 2-chlorotoluene. Moreover and even worse, chlorinated dioxins will form from the familiar though out-phased polychlorinated biphenyls (PCBs) upon irradiation.

38) The corresponding redox potentials of these ions are about +2 V vs normal hydrogen electrode (NHE; pH = 0), so there is just kinetic preference against oxidation of water which is present in large excess, of course. Ag^{2+} even is capable of oxidizing O_2 and xenon in cold, acidic, non-aqueous and non-oxidizable fluorophoric solutions (Klapötke and Tornieporth-Oetting, 1995)!

39) Note that here the carboxylate anion undergoes photocleavage of some substituent whereas “unsubstituted” carboxylates do not undergo any photoreactions (only neutral R-COOH undergo loss of CO_2 or CO_2H radicals [Mittal, Mittal and Hayon, 1973] at somewhat shorter wavelengths).

- 4) Another way toward mineralization of organic pollutants is their *combustion*. Dioxines and dibenzofuranes—like chlorofluorohydrocarbon (CFHC)—undergo complete destruction if in contact with red-hot carbon, that is, by co-combustion in a coal-power plant, leaving behind only CO₂, water and alkali or alkaline earth halides.
- 5) *Photoelectrochemistry*—in its classical way—provides a combination of oxidative and reductive processes.⁴⁰⁾ Concerning environmental chemistry, all mineralization of various kinds of organic contaminants, detoxification of alkylmetal compounds by R cleavage and of As(III) by oxidation were demonstrated. Some toxic noble metals can be removed from solutions by photoelectrochemical cementation (precipitation of pure metal like with Cu, Ag, or Pd).
- 6) “*Fluid combustion*” is achieved using supercritical water vapor at $p \approx 300$ bar and temperatures of 400–650 °C. Under these conditions, beyond the critical data of water, water is a gas and thus miscible with every other gas, including dioxygen, but, being almost as dense as a liquid owing to the high pressure,⁴¹⁾ produces considerable solvation, taking up unpolar organics, also. The rates of hydrolysis of, for example, esters or amides become very large, with dioxygen causing oxidations (except for the upper end of the temperature range, where direct oxidation of CH₄ and higher hydrocarbons by water according to $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2$ etc. does not occur⁴²⁾).

Methods which draw upon redox processes meet the common difficulty that there is no linear or even only parallel relationship between redox potential and toxicity of produced speciation forms among different elements, with mixtures of pollutants quite common in practical cases. Hence trying to produce some extreme value of redox potential—either oxidizing (anode, but also with water chlorination) or

40) Of course, cross band gap excitation produces equal numbers of conduction band electrons and valence band holes (where electrons are missing) in any semiconductor, regardless of its chemical identity and possible doping, just for reasons of charge conservation. As long as the semiconductor is stable, not undergoing photocorrosion, both kinds of charge carriers will eventually turn up at some outer interface of the particle and react with substrates there. However, the speed of charge propagation depends on semiconductor and doping, being equal only in few materials (e.g., undoped elemental germanium, AlP or AlAs). The problem of unwanted electron reactions can be resolved by relocating light absorption and hole production into some

sorbate layer made of metal complexes (Fränzle, 1996; Kokorakis *et al.*, 2000).

- 41) At T_c and p_c , solvents have about one-third of their ambient-conditions density. In a colloquial supercritical system, the temperature is not much higher than T_c , but the pressure usually exceeds p_c considerably. Hence the density will be $> \frac{1}{3} \rho_{\text{normal}}$; and hence there is considerable solvation, but no dissolution of common salts as supercritical solvents are unpolar solvents. However, this allows the mixing of long-chain hydrocarbons and O₂ in water for “fluid combustion”.
- 42) Amino acids other than glycine, alcohols and so no decompose in hot water already much below the critical point producing H₂, carbon oxides, carboxylic acids and NH₃ (Schulte, 1999).

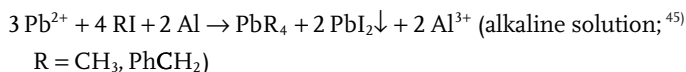
reducing (cathode with large hydrogen overpotential, solvated electrons in liquid NH_3 , amines) –, be it by “purely” chemical means, electro-, photoelectro- or even radiochemistry (production of hydrated electrons, conversion of these into OH radicals⁴³), will include some risk of producing highly toxic intermediates from some components of the pollutant mixtures even when detoxifying most of the others. If so, intermediates must be kept safely from escaping the reaction chamber of remediation. Otherwise, the (frequent) case of mixed contaminations, for example, a mixture of As(III) or organotins with heavy-metal compounds (the toxicity of which increases upon oxidation of the mixture) calls for a secondary or even multi-step treatment of the reaction mixture.

By superposition of the Pourbaix diagrams for the corresponding elements and their toxicological data, some “window” of acceptable compromise conditions can be identified for the purpose of both immobilization and detoxification. One-step clean-up can only be achieved if the optimal speciation forms will stably coexist. For example, in the wastewaters from leather-making and dyeing, which (at least in earlier times) used to combine chromate with residues of As, Ni and other elements, it is necessary to ensure complete reduction of CrO_4^{2-} without reducing AsO_4^{3-} by an appropriate redox potential, unless the redox potential is taken so far down as to produce elemental As.

Whereas organotins react readily at anodes (Stichnothe *et al.*, 2005), certain other element–carbon bonds (e.g., bonding to As, Tl, Hg, Si or F) may be both toxicologically relevant and highly stable, even allowing for extreme redox potentials and/or attack by chemicals like concentrated nitric acid.⁴⁴ Such compounds can be readily formed by both fungi (moulds, in particular) and various microorganisms; besides, bioalkylation of certain elements was also detected in mammals (for man, e.g., As and Bi; Hollmann *et al.*, 2010) and Hg^{2+} can formally abstract R^- (carbanions) from many organoelement compounds including silicones, producing extremely toxic RHg^+ ions. The familiar light-metal technical materials themselves form only organometals which violently hydrolyze and react with air. Nevertheless, in aqueous environments, they (e.g., Al) can bring about formations of the hydrolytically stable but more toxic organometals (e.g., lead tetraalkyls) from metal salts and organohalogens in some cases (Ahmad *et al.*, 1980):

- 43) 1) radiolysis of water: $\text{H}_2\text{O} + \gamma \rightarrow \text{H} + \text{OH}$, then (in alkaline solution)
 2a) $\text{H} + \text{OH}^- \rightarrow \text{e}^-_{\text{aq}} + \text{H}_2\text{O}$
 2b) $\text{N}_2\text{O} + \text{e}^-_{\text{aq}} \rightarrow \text{N}_2 + \text{OH}$ or (in acidic solution)
 3) $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$
- 44) Concerning As, trimethyl arsane (Gosio gas) in the atmosphere is not mineralized into inorganic As in the atmosphere and hydrometeors, notwithstanding the joint attack of UV radiation and OH radicals; rather the dominant As compound in

rainwater is cacodylic acid (dimethylarsinate), having lost just one CH_3 group. Concerning thallium, the $(\text{CH}_3)_2\text{Tl}^+$ cation (Schedlbauer and Heumann, 2000), which can be produced by certain bacteria (Thayer, 1995), is so stable toward both UV and even prolonged boiling in 70% nitric acid (!) (Elschenbroich and Salzer, 1988), that it is hard to explain why there are any other speciation forms of Tl in the ocean, actually.

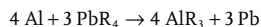
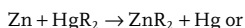


To understand these non-linear changes of toxicity experienced when changing ambient redox potentials and how to deal with them, consider the above example + nitrogen as cuts through the Pourbaix diagrams at constant pH = 7.5. The rodent toxicity of the inorganic speciation forms of N, Cr, and As all vary upon changes of their redox potential (Figure 1.6).

In systems dynamics, concerning both mechanical and chemical systems with some feedback features, for example, in the double pendulum, in celestial mechanics (feedback by mutual gravity attraction) or in chemical oscillators (feedback by autocatalysis of formation of some reaction intermediate), oscillatory, pendulum-like behavior—also suggested to occur in population dynamics—will not simply impose some periodic or quasi-periodic perturbation on otherwise linear kinetics to produce a sine-like modulated linear process. Rather, something quite different will happen: chaos (May, 1976); in fact, chaos was first noticed to occur in celestial mechanics (by Laplace—already around 1800!). In deterministic chaos, deviation from the predicted, unperturbed trajectory increases with time in an exponential manner which is neither predictable nor reproducible in repeated runs of the experiment (e.g., a planetoid subjected to chaotic track perturbation by the interaction of, with and among several larger bodies may appear anywhere in the Solar System or may get ejected altogether), chemical oscillators, rather than producing periodic changes of state variables (pH, redox potential, optical spectra) over few or even hundreds of cycles, then lose any foreseeable kinetics after initial period doubling.⁴⁶ Chaos accordingly refers to apparently erratic, unpredictable changes of concentrations or abundances of certain actors involved in the system—even biological species—and correspondingly of kinetics (as the latter refers to the consumption or production of some intermediate species. For some period of time, it was outright fashionable to attribute features of deterministic chaos to quite diverse kinds of systems with any mode of feedback involved: non-periodic mass

45) This reaction is remarkable for at least three reasons:

- 1) Organoaluminum compounds forming from Al and RI spontaneously ignite in air and violently hydrolyze.
- 2) As was already discovered by Edward Frankland (1825–1899) in the 1850s, in some inert solvent, mixtures of alkyls or aryls of rather noble metals, for example, Hg, Cu but also Pb, react with metallic Al or Zn or Mg exactly like halides of the above more “noble” elements would do, thus destroying the products which are found to be stable here (i.e., in water), for example,



- 3) Organolead compounds are extremely neurotoxic (this is the reason for ecological relevance).
- 46) These are no oscillations around chemical equilibrium; the final approach of some chemical oscillator toward equilibrium occurs in a classical, linear manner in every case. “Real” chemical chaos yet is rare, requiring multiple feedback modes like those possible in oxidations of thiocyanate ion ($\rightarrow \text{HSO}_4^- + \text{HCN}$), the paradigmatic system being the ClO_2^- chlorite-based oscillator which oxidizes SCN^- (Doona and Doumbouya, 1994), $\text{S}_2\text{O}_3^{2-}$ or thiourea.

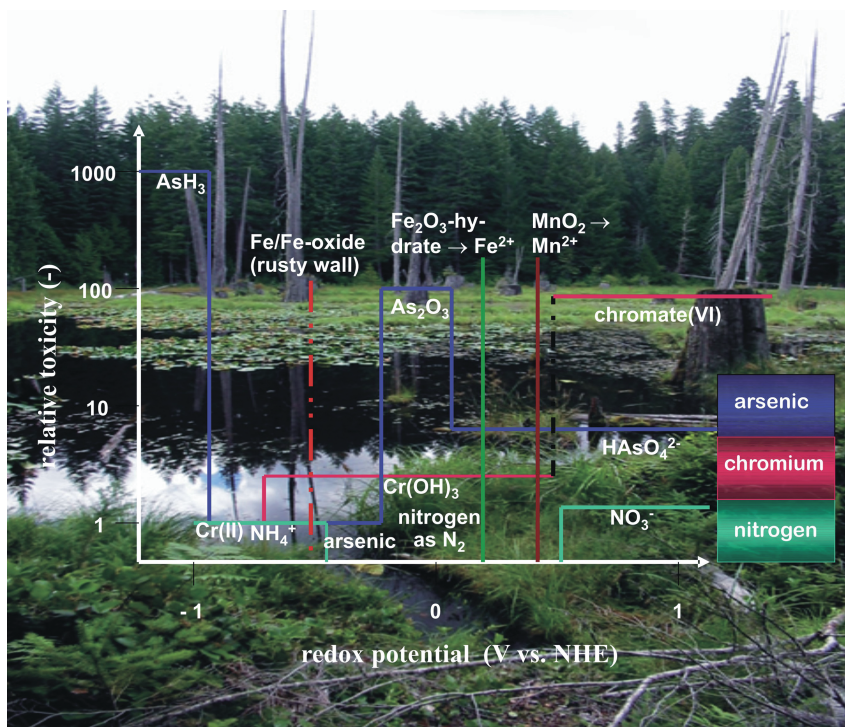


Figure 1.6 Dependence of relative (rodent, oral) toxicities of three elements N, Cr, and As of redox potential of soil or groundwater. A “rusty wall” made from iron (Fe filings dispersed by sand or gravel) accordingly is

best suited to minimize the toxicities of all three elements (background photograph courtesy of Wind River Company Crane Research Facility, USA; scheme overlaid by the authors).

abundances of migratory locusts or of lemming voles were interpreted as signs of chaos, and so were apparent breakdown of some catalytic chemical systems, stock-exchange crashes and many others. Concerning environmental technology, chaos appears both in certain, additionally photochemically perturbed reaction sequences and in technical oscillations. Chaotic dynamics of populations—if they actually exist—would pose some severe problems in biotechnological plants of various kinds, for example, for sewage treatment or bioremediation.

When analyzing or designing some device of environmental technology and its modes of operation, quite a number of different approaches are at hand. They are not only grossly different with respect to complexity of comprehension (somewhat alleviated by the option to use standard modeling software for chemical engineering nowadays—perhaps without really understanding what you are doing . . .), but also concerning the “response” of the modeling procedure toward the reduction of complexity: if you omit some features or leave aside some partners of a feedback loop, can you still make sure (by some general mathematical proof) that the model you chose to use will reproduce the actually observed dynamics, exotic as they

might be? Maintaining the principal behavior, for example, oscillations or exponential growth, in this “reduced” model obviously *suggests* you conserved the features and subsystems which are in charge of “exotic” dynamics but you still have to give proof that this assumption actually applies.

Some of these models, extracting features of autocatalysis combined with the topology and sign (negative, positive) of feedback loops from a “background” of “boring” linear processes (stoichiometric network analysis, SNA; Clarke, 1974, 1980; Eiswirth, Freund, and Ross, 1991a,b) were used by these authors (Fränzle and Markert, 2000a,b, 2002a,b, 2003, 2007; Fränzle, 2010) to work out the results of autocatalysis (in biology, reproduction) from the background of other events in metabolism or even in entire biocoenoses or ecosystems. An advantage is their sometimes more straightforward approach into complicated feedback dynamics, as compared to classical computer simulations of feedback. Even if this is “open-source” code, the interested colleagues—and more so decision-makers and stakeholders—must rely on (in effect, just believe in) the correct implementation of the corresponding assumptions in the code (but this cautionary remark also holds for simulations in architecture statics or aircraft aerodynamics!). Yet, qualitative arguments from SNA—which is by no means restricted to chemical or biochemical systems, but also applies to nuclear fission energy, astrophysics and other topics (Clarke, 1980)—were successfully used both in ecological planning and in understanding long-term large-scale dynamics in economy (Kondratieff-type long waves; Grossmann *et al.*, 1997; Fränzle and Grossmann, 1998).

When looking for possible causes of identical kinds of damage to the biota, such as chlorosis in green plants, it still remains difficult to obtain sufficient pieces of information for pinpointing the actual cause of some problem: when some species x (plant or animal, etc.) in some forest area y rapidly declines in number, what is this due to? Is it the impact of heavy metal a , herbicide b , virus c [such as both Ebola and simian immunodeficiency virus (SIV, causing AIDS in apes) in the decline of the great apes in Central Africa], some predator d which was released there or immigrated in unusual conditions (such as wolves passing the ice cover of the Great Lakes in 1948 to invade an island which hitherto had been a riskless though overused habitat for thousands of mooses, reducing the latter to some 25 at first) or is it due to “bad weather” (e , which may introduce geochemical consequences also), rather than “bad luck” in the realm of chaotic dynamics? Five variables in this example (a – e ; counting heavy metals and viruses as one single cause each, which is obviously oversimplified) demand five independent investigations—difficult enough to get in field studies—varying one parameter only per study. Even then, you end up with mathematically meaningful statements on just one species and its responses, one of very many which interact⁴⁷⁾ in a biocenosis.

47) Cf. the experiments on population dynamics in small temperate lakes in Canada (Sterner and Elser, 2002): (i) removing all the top-level piscivorous predators by fishing, exclusion (fences) of bears or otters, (ii) adding certain chemicals or (iii) manipulating the C/N/P ratios of dissolved and particulate organic

matter suspended in these water bodies and investigating the effects on populations of zooplankton and planktivorous fishes. Some of the latter effects are both seemingly paradoxical and hard to distinguish from each other, making causal analysis in real-life systems next to impossible.

When you eventually cast your assumptions or empirical “if–then” statements on the systems and its dynamics (population, chemical, etc.) into a model using partial differential equations to study the dynamics, you end up with systems of coupled equations which can only be solved when there are *at least as many* independent equations (with each one representing one fully characterized experiment or field study) as there are different variables (five in our oversimplified example). Accordingly, except when looking for the specific inhibition of porphyrin biosynthesis, the analytical determination of, for example, Pb in some bioconiosis or biogenic sample thus tells you almost nothing, let alone the question whether this lead is excluded from bioresorption by being precipitated as sulfide (galenite), sulfate, chlorophosphate or carbonate in the sediment, or becomes both lipophilic and neurotoxic by bio- or anthropogenic alkylations. *Speciation*, of course, is a chemical criterion. Metal ions, for example, might occur as mixed-oxide particles, aqua- or ligated complexes, bound to dissolved organic matter (DOM), biomass and in other forms. A classical hypothesis (Shaw, 1961; Bienvenu, Nofre, and Cier, 1963) which also made its way into ecotoxicology (Lewis *et al.*, 1999; biotic ligand model; Santore *et al.*, 2001; Paquin *et al.*, 2003) postulates the critical property of a “cocktail” of metal speciation forms around some organism to be the concentration (or, rather, chemical activity) of the “free”, that is, aquated ion. This assumption, called the free ion activity hypothesis (FIAH), was derived by noticing that simple salts or labile complexes of metals are⁴⁸⁾ much more toxic than stable complexes containing the same metal ion. According to FIAH, it is the free ions which interfere with metabolism, for example, by replacing essential metal ions in metalloproteins or reacting with disulfide bridges to destroy protein tertiary structures. In some stable complexes, like hexacyanocobaltate, it is almost impossible to cleave the “shroud” of cyanide ions to uncover the Co^{3+2+} ion which thereafter could become toxic. Unless the very ligands are used or else degraded by biomass itself, this barrier would hardly be passed. Part of the difficulties met by FIAH are due to the often pronounced changes of relative stabilities of various complexes when the metal centers undergo redox reactions.

1.3.2

Substances and Their Sources

Chemically most diverse substances get into the three environmental compartments air, water and soil steadily. Possible sources include biological, geological (erosion, weathering, volcanoes) and other natural events such as forest wildfires but also—to a substantial extent—human activities like agriculture, industrial activities or traffic. Natural and anthropogenic trace gases and their respective sources are discussed in more detail in Section 2.2.1. If the compounds passed into the environment do not undergo fast chemical

48) There are different exceptions to this empirical rule, mostly with respect to the uncommon oxidation states of some metals, like the extreme toxicity of neutral

metal carbonyls like $[\text{Ni}(\text{CO})_4]$, or the toxicity problems associated with fluorocomplexes, including very stable ones.

changes,⁴⁹⁾ they undergo transport and distribution/partition among the environmental compartments. Otherwise, if there is high reactivity and hence a short lifetime of the primary substance, the above statement will likely hold for their long(er)-lived reaction products.

What does promote corresponding reactions? The principal driving force for both transport and partition of the chemical inside and among environmental compartments are chemical gradients, including those of temperature as well as pH differences among some water bodies and the underlying or surrounding sediments. These may influence the partition of both acidic and alkaline species, including metal ions. Even if the corresponding gradients are absent, partition will take place due to adsorption or similar equilibria when particles get bound (adsorbed) to particles and then transported or deposited in this solid state. Substances listed in Table 1.3 can be grouped, for example, according to:

- Volatility;
- Tendency to change or be moved into some other environmental compartment than that they were produced or released in(to). A further criterion for grouping considered in Table 1.3 is:
- Persistence.

As a rule, inorganic, degradable and persistent organic compounds are distinguished. Of course, the difference among the latter two is quantitative rather than qualitative, floating and subject to definition; in addition, inorganic gases and anions (may) also undergo oxidative or biological degradation or bind to soil components in an irreversible manner by, for example, complex formation. For example, both ammonia and cyanide are processed by certain organisms (nitrification, i.e., NH_4^+ oxidation eventually to yield NO_3^-) even though they are toxic for most others and many excrete them. NH_3 , SO_2 and CO are too short-lived (weeks to few months in troposphere) to undergo global transport, which means their transport ranges are limited rather than global. Like organic compounds, heavy and light metals can be partitioned into all environmental compartments and biomass.

After being emitted into one environmental compartment, substances undergo partition among the three compartments according to their chemical properties. Salts, for example, will (possible, at most) dissolve in water or groundwater, while aerial transport is feasible in aerosol only. Volatile organic compounds are readily moved by wind but get strongly adsorbed to soil, while their behavior in water is

49) "Not undergoing chemical changes" here allows for reversible processes through, for example, the dissociation of (volatile) organic or inorganic acids when dissolved in water. Although acetic acid (partly) dissociates in water, it can be distilled from aqueous solution when and because it can return into a molecular, volatile state due to the acid/base equilibrium (formic

acid, HCOOH , a considerably stronger acid than CH_3COOH , also is a component of the [mainly polluted] atmosphere which is in equilibrium between the gas phase and rain drops, and the same holds for HCl , HNO_3 , although these display far more dissociation in aqueous solutions [gas phase levels of all three: ≈ 1 ppbv]).

Table 1.3 Kinds of pollution and pollutants in the different environmental compartments (from Markert and Friese, 2000, with modifications from Förstner, 1995).

Environmental compartment	Bound substances	Examples	Source(s)
Water	Degradable organic compounds	Fecal matter, tensides, solvents, pesticides, chemicals used in technical processes, fats, oils, soluble residues from plant or animal origins, fundamental chemicals, intermediates and terminal products	Town, villages, domestic uses, agriculture, textile processing, metallurgy, painters, food, chemical and paper industries, waste dumps
	Persistent organic compounds	Tensides, solutions, pesticides, commercial chemicals, basic chemicals, intermediates and terminal chemical products	Agriculture, textile processing, metallurgy, painters, chemical and paper industries, waste dumps
	Inorganic compounds	Heavy metals, salts, cyanides, chromates, fertilizers	Metallurgy, metal huts, leather production, towns and settlements, agriculture, waste dumps
Soil, sediments	Degradable organic compounds	Fecal matter, pesticides, residues from plant or animal origins, fundamental chemicals, chemicals used in technical processes, intermediates and terminal products, sewage sludge	Agriculture, domestic and toxic waste dumps, waste disposal facilities
	Persistent organic compounds	Tensides, solvents, pesticides, commercial chemicals, fundamental chemicals, intermediates and terminal chemical products	Toxic and industrial waste dumps
	Inorganic compounds	Heavy metal compounds, salts, ashes, sludges	Waste dumps, waste incineration facilities, metal production
Air	Organic gases	Solvents, hydrocarbons, volatile pesticides, volatiles from industrial chemistry	Painters, refineries, agri- and aquaculture
	Inorganic gases	Carbon monoxide, hydrogen chloride, sulfuric acid, nitrogen oxides, ozone, metal vapors, carbon dioxide, ammonia	Combustion chambers, incineration plants, engines, industry, NH ₃ , also from agriculture
	Dust(s) and smoke	Metal oxides, PAHs, soot	Metal production, waste incineration, combustion plants in general

dictated by both (aqueous⁵⁰) solubility and adsorption tendencies. The quantitative relationship is given by partition coefficients, for example:

$$K_{\text{sediment/water}} = \log\{C_{[\text{substance in sediment}]} / C_{[\text{substance in H}_2\text{O}]}\} \text{ (equilibrium assumption)}$$

One must distinguish three different scenarios, namely:

- 1) Enrichment/accumulation in sediment,
- 2) Comparable shares of compound in either environmental compartment and finally, the opposite, that is:
- 3) Extraction of something from aquatic sediment into the water column above it.

The latter is likely when some river or wind-agitated standing water body uncovers sediment layers which took up pollutants long before by erosion or when compounds are passed into water which participate in extraction by, for example, complex formation [with a ligand like ethylenediaminetetraacetic acid (EDTA) being added, see also Section 4.2.2] or nonpolar liquids spilled into water. Of course, partition coefficients depend not only on the composition of the solid phase but also on the properties of water such as pH (the distribution/partition of anions of longer-chain carboxylic acids or of phenols differs considerably from that of neutral compounds), ionic strength or the presence of tensides (including biogenic ones like certain fragments of cells or lecithine). Yet there are empirical relationships to $\log k_{\text{OW}}$, permitting an extrapolation from known behaviors of few substances in a water/sediment biphasic system to the adsorption of others, including possible ecotoxicological risks.⁵¹

Some (in fact, rather many) of these substances are emitted exclusively by man—be it on purpose, as with pesticides or tensides (washing detergents) or by accident (*products* from crude oil). Many more substances are released both by nature and anthropogenically (including NO_x , SO_2 , HCl, Hg and CdO from both fossil-fuel-combusting power plants and volcanoes), with one or the other prevailing; only recently we started to appreciate which “strange” compounds are produced particularly by aquatic animals, including, for example, halocarbons, isocyanides, “mustard oils” (R-NCS) and even (bromo-hydroxy)dioxines. Substances from anthropogenic activities cover by-products of combustion or metallurgy (huts, smelters) as well as metabolites from man and husbandry or commercial chemicals, especially volatile solvents. Among the substances from both man and biota or geological sources are inorganic and organic gases like HCl,

50) Aqueous solubility of organics is linked to $\log k_{\text{OW}}$ by an empirical formula which essentially states solubilities in 1-octanol will not differ considerably, and adsorption of organics to soil/aquatic sediment rather behaves according to $\log k_{\text{OW}}$, also. Hence aqueous solubility is directly linked and related to adsorption. A tendency in organics such as adsorption will increase

among such compounds which do not at all readily dissolve in water.

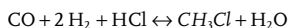
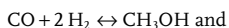
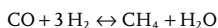
51) Organisms like the sediment-dwelling worm *Tubifex* spp. accumulate certain compounds taken from sludge. *Tubifex* in turn are eaten by fishes and water fowls (e.g., ducks), passing the contaminants back into ambient water as well as into the trophic chain up to man.

CH_3Cl ⁵²⁾ and CH_3Br , both also solids like certain metal oxides from either smelters, wildfires or erosion.

Anthropogenic inputs and natural (other than biogenic) ones differ as follows: Humans produce and use items with considerable affordances of materials and high chemical complexity or diversity: while hardly any kind of organism does need more than 25 chemical elements, a colloquial personal computer makes use of many more elements. Already when raw materials, precursors and spareparts are produced, lots of matter are moved, relocated and processed,⁵³⁾ going far deeper into soil than any plant root would be able to do, producing and partly emitting all heavy metals, salts, oxides of carbon, nitrogen and sulfur, dusts, wastewaters carrying sediments and dissolved salts plus processing chemicals—including cyanide—in much larger amounts than any other living being can afford for producing its biomass,⁵⁴⁾ most of it getting into the environment somehow and somewhere (“ecological rucksack”⁵⁵⁾). As long as the product or device is operated, it keeps (directly or indirectly, e.g., associated with production of electrical energy used by it) emitting “waste” matter into the environment, be it by consuming/ converting energy (e.g., in traffic systems, heaters), by mechanical wear or simply since the device itself produces or processes some chemicals (apart from atmospheric O_2 , fuels) besides consuming energy.

Eventually components which can no longer be used, and are hard or inconvenient to recycle, are brought to deposit pits (dumps), both official (legal) and non-official ones. There they can cause secondary emissions. Passing some stuff to the environment can even be part or scope of its use, for example, the domestic function of tensides is the dispersion and transfer of some solid or liquid pollutant to the environmental compartment water or pesticides (if used in agri- or aquaculture directly rather than in storage). Except with water-based dispersion colors, the drying of paints entails the release of solvents which—regardless of whether these paints are distributed indoors or outdoors—make their way to the atmosphere also. Landfills and other waste dumps influence the third environmental compartment,

52) Methyl chloride is also formed besides CH_4 in volcanoes which emit rather reducing (containing appreciable [excesses of] CO , H_2 , CH_4 , and H_2S) gas mixtures (e.g., on Kurile Islands and adjacent Kamchatka Peninsula), probably by some variety of methanation reaction in cooling gases, with ash acting as a catalyst:



53) Whereas plant roots or cave systems dug by animals extend to some 10m below the surface at most, mining is done down to 4km, crude oil and natural gas production even to >7km below the surface.

54) While animals use some 5–10 times of the biomass produced, and plants give away several times the amounts of minerals to be resorbed as ligands into soil, an average citizen of an industrialized country will consume some 10000 times his or her weight during their lifetime from fossil fuels alone.

55) The ecological rucksack or “footprint” (Schmidt-Bleek, 1992) gives the ratio of weights between the total mass moved in mining plus that used in processing (e.g., coke burned in a high kiln during iron production) divided by the weight of the final item produced and eventually used. For example, if 2 g of gold are extracted from 1 t of ore (a quite modest yield), the rucksack will be 500000.

soil, both by geochemical influences and because forming an underground disposal site necessarily implies excavation which inevitably destroys evolved soil structures.

Even if liquid, solid or even radioactive residues are correctly disposed of in depositories, permanent seclusion from environmental compartments cannot be taken for granted: biological processes in anaerobic conditions can methylate semi- or heavy metals (As, Sb, Se, Hg, etc.), reduce (Hg; Wood, 1975) or carbonate them (Ni, Mo, W), each process producing volatile products which may be vented along with disposal-site gases; leaks or underground barriers which are not at all sufficient will entail matter transfers into soil and groundwaters. Besides the above highly toxic products, landfill gases contain some 1% of benzene (i.e., comparable with car exhaust gases untreated by any exhaust gas converter!) formed by biochemical reactions involving aromatic compounds. Internal combustion engines of whatever size, including power plants and heating systems, first interact with the air by obtaining oxygen for combustion therefrom, afterwards passing “waste gases” and particulate byproducts (fly ash, dust, soot) into the air again. These solid particles are going also to be deposited on both soil and water surfaces.

Volatile compounds are going to be rapidly transported in the atmosphere; those soluble in water are moved with it in rivers, tidal streams or ocean currents. But substances which are neither really volatile nor soluble in water beyond, say, 10^{-7} g/l can become subject to fast transport too provided they get bound to (sufficiently small) particles, that is, aerosols or particles suspended in water. While persistent compounds (and element species such as noble gases, Hg vapor, or elemental sulfur) simply follow partition equilibria when spreading beyond that environmental compartment they were emitted into, reactive species behave differently, according to (usually unlike) rates of chemical alteration and partition equilibria for the secondary product(s).

For example, non-polar organic substances will stick by adsorption to likewise non-polar solid phases like humic matter, soot,⁵⁶⁾ less to polar sorbents such as silica or clays. Benzene or PAH substitution by one single hydroxygroup will increase aqueous solubility by a factor of 15–20 from benzene, naphthalene, phenanthrene and so on to the corresponding phenols, naphthols, hydroxyphenanthrenes and so on, in the same turn decreasing $\log k_{ow}$ by 2 or more, thus also changing their tendency toward the adsorption to (mainly organic) “mud”. If either photo- or biochemical processes (attack by photoproducted OH radicals, activity of laccases and other enzymes) bring about the hydroxylation of non-persistent compounds, their partition among soil, air and water or among different phases or fractions of soil will change also. After reactive compounds are passed into one

56) This is the reason for the particular toxic and carcinogenic risks associated with soot from combustion: the solid, polymeric support—something in between graphite and graphene—does not pose substantial toxic problems for itself, but it perfectly

adsorbs those PAHs some of which are involved as intermediates in its very formation, including highly carcinogenic tetra- or pentacyclic ones such as chrysene, benzo(a)anthracene and benzo(a)pyrene.

environmental compartment, their secondaries—which need not at all be less hazardous to environment and biota—might pile up in any of the other two. Besides benzenoid or (smaller, volatile) PAH aromatics, this does likewise hold for aliphatic compounds such as alkenes or some inorganic species: chromates in water or soil can be reduced to Cr(III), then precipitated by, for example, phosphate, markedly reducing both their mobility and toxicity. Semivolatile but highly persistent compounds ($T_{1/2(\text{troposphere})} > 5$ years) undergo global distribution by air-flows until getting trapped by “global distillation” in cold traps like arctic or high-altitude regions, or they make their way into regions where the environment is sufficiently aggressive to enforce chemical transformations eventually, through chlorofluorohydrocarbons (CFHC) and their photolytic products in stratosphere, (allowing for photolysis at $\lambda \leq 240$ nm rather the surfacial 295 nm limit).

While the mobility of substances is very small inside soil, the production and transformation rates are high owing to the remarkable biological activities there. Geochemical pedogenesis (making soil from primary sediments or stone rubble) is also associated with pronounced transport of matter during eolian and water erosions, sedimentation and redox processes due to species which get there from either the soil–air interface or from groundwater.

The list in Table 1.3 also mentions a larger number of biogenic residues, ranging from animal and human manure, fecals over residues from cattle breeding and agriculture to oils or fats (gases like ammonia, liquids like manure and solids including entire carcasses, besides parts of plants, food- or fodder-making residues. One only gets a realistic idea what does happen here if one is aware that almost 50% of all the photosynthetic production on Earth (including oceans and arctic regions) are used or even “organized” (agriculture, forestry, cattle and fish breeding) by man for his own purposes or get caught (quite literally) without being the objective but nevertheless most likely to die in this process (“by-catches” in fish-, shrimp production, with the by-catch often corresponding to 5–10 times the “actual” prey). These 50% correspond to billions of tonnes per year, with respective challenges to extent of biological degradation of these huge flows of reduced organic matter (straw, sprouts or bones can only be partly used in agriculture again directly). Biogenic water-soluble residues pose a burden to ambient waters and (before) a challenge to technical environmental chemistry in sewage treatment plants, and so do insoluble kinds of waterborne waste (lumps of fat, large-scale organic particles, torn cellulose, plastics). Although these are removed in the first, mechanical part of a sewage treatment system already, they must be destroyed somehow thereafter, yet. Whereas combustion of biogenic residues might be attractive for releasing quite substantial amounts of energy (power plants using straw or wood fragments/saw dust/pellets or biogas), biogenic organic matter, for being biogenic, does contain all the other elements involved in biology besides C and H (and many more) which inevitably are released upon combustion, adding pollution hazards (ash, NO_x , SO_2) to the consumption of oxygen from air now (rather than of dissolved O_2 from water).

An attempt to make a mass balance is most telling: unplanned emissions outweigh purposeful inputs by orders of magnitude, with the largest ones of the

former being several bio. t/year of CO₂ and—still—large amounts of evaporating solvents, also capable of producing substantial problems due to halogen contents and an IR radiation absorption far in excess of CO₂, in addition there are N oxides (N₂O and others) and CH₄ from agriculture (degradation of excess nitrate fertilizer, rice paddies and cattle breeding, respectively) and from disposal sites (about 10⁸ t/year each).

This compares to a “planned” input of some 110 mio. t of NH₃ (in 2002) in ammonium salt fertilizers, some 10 mio. t of tensides⁵⁷⁾ and similar amounts of pesticides (total weight of formulations rather than “pure” active agent—the latter was 2.6 mio. t in 1995). The largest amount of tensides is used in oil production now, besides domestic cleaning, ammonia undergoes biological oxidation to form nitrate eventually; both the original compounds and their secondaries undergo transport and partition among the environmental compartments. Of course, tensides are going to influence this partition considerably (which is their practical purpose, after all).

1.3.3

Transport and Chemical Alteration of Environmental Chemicals

Table 1.4 shows that there are different ways of transport and transfer of chemicals in and among environmental compartments, for example, by advection (transport making use of fluid flows), diffusion, dispersion (spreading on some water surface) or transport by particles. Neither diffusion nor dispersion have certain typical ranges of speed which would allow to predict the prevalence of either transport mode or of advection in a general way, except for advection dominating over large distances. Brownian (molecular) motion occurs in random direction, causing the time to cover a certain distance to increase with the square of that distance.⁵⁸⁾

Advection refers to horizontal transport in and effected by air or water, that is, wind or water currents. While typical wind speeds are 5–7 m/s, rivers and ocean currents including tidal flows rather proceed at 1–2 m/s. Thus substances, either

57) A rough estimate which is based on the following substance-specified data on production and consumption:

- Straight linear chain alkylbenzene sulfonates which are the backbone of most anionic tensides 2.6 mio. t (in 2000);
- Fatty alcohols (long-chain primary alcohols like cetyl alcohol [*n*-hexadecanol] or polyethylene glycols 1.6 mio. t [in 2000]);
- Tensides made from crude oil/ petrochemistry constituted some 0.1% of total crude consumption in 2002 whereas about 50% of tensides were made from biogenic fats or oils

(which include classical alkali carboxylate soap).

- 58) In many old-style chemistry lecture halls there are vertical liquid-filled glass tubes to visualize the rate/slowness of diffusion, using solutions of colored salts (permanganates, [Cu(NH₃)₄]²⁺) which take years (≈10⁸s) to pass 1 m, with the progression of diffusion fronts going on with the square root of time which has passed by. Hence, 15 nm in a synaptic gap is covered within milliseconds at most during nerve activity. Hence in groundwater, diffusion is significant only when there is no (reason for) macroscopic flow (typically 5–10 m/year) or if very short distances are concerned (<1 cm).

Table 1.4 Processes involved in transport and removal of chemicals after they get into the environment (after Fent, 2003).

Type of process	Specific process	Chemicals concerned (examples)
Transport	Advection, diffusion, dispersion	Crude oil, atrazine
	Particulate transport	PAH
Transfer	Dissolution in water	Tensides
	Adsorption to particles, sediments and soil	Heavy metals
	Evaporation into atmosphere	Tetrachloroethylene
Transformation	Atmospheric deposition	N and S oxides, dioxins
	Abiotic (hydrolysis, photochemistry, redox reactions)	Organophosphate pesticides
	Aerobic or anaerobic biological degradation	Methylmercury cation, pesticides

dissolved or particulate, can be transported across continent-size distances within a few weeks' time.

Atmospheric flows are then directed mainly in West–East or converse directions whereas ocean currents mainly propagate South–North at the surface and counterwise in the deep ocean (e.g., Gulf, Humboldt, Benguela currents). Thus the most reactive, shortest-lived compounds which make their way to globally equal distribution although they are emitted in certain parts of the Northern hemisphere mainly, are methane and methyl chloroform ($\text{CH}_3\text{-CCl}_3$) at some five years tropospheric lifetime.⁵⁹ Volatile or gaseous compounds with similar or even longer lifetimes accordingly undergo global distribution also, eventually possibly to be precipitated in “cold traps”. More reactive substances (tropospheric lifetime <6 months) like CO pass neither pass the tropopause vertically nor make it to the other hemisphere horizontally through the calm belt along the equator.

The atmospheric transport of some substances is obviously terminated by deposition, notwithstanding subsequent transport in and by water. Compounds which are readily soluble in water will be deposited by rain, fog or snow within days, limiting the ranges of transport to about 1000 km. Given the usual direction of winds in Europe, it is obvious why during the 1980s massive emissions of SO_2 from certain states or parts thereof (United Kingdom, the former German Democratic Republic, the eastern ČSSR) would hit next or second-next neighbor states

59) Lifetimes can be estimated from the reaction rates with OH- and (during the night) NO_3 radicals and rates/quantum yields of photodegradation by light of $\lambda \geq 295$ nm.

mainly, separated from the emission sites by small seas at most (southern Norway and Finland, parts of Poland and Byelorussia), with this medium-range transport aggravated by “high smoke-stack policy” with stacks of up to 400 m height keeping the immediate regions clean but producing essentially laminar waste gas tracks no longer exposed to turbulent mixing which would be caused close to any rough surface in settlements or forests alike.

While transfer in water will occur in either adsorbed or dissolved forms, matters are different in air because all gases can be mixed indefinitely. Without mixing limits like among liquids or solids, the only “problem” might be the chemical (reaction) formation of aerosols (ammonium salts, Los Angeles Smog, including peroxide-induced formation of organic oligomers). However, adsorption to solid particles is very similar in either kind of fluid; such particles can be transported over continental distances if they are small enough (their density is much in excess of that of air in any case), for example, the almost proverbial Saharan dust which provides most of the Fe and Mg supply of Amazonia.

So far, these processes are merely physical ones, except for some reversible chemical reactions like protolysis with acidic or alkaline (NH_3) gases or vapors, but then transformations happen which irreversibly change the chemical identities of these substances, including both abiotic (hydrolysis, photolysis, redox reactions) and biotic processes among which latter aerobic and anaerobic ones might afford the same intermediates. The same holds and is repeated for the secondary products, which undergo transport and transfer quite like their precursors emitted originally but of course with different kinetic and physicochemical parameters. While there is no fundamental difference among the processes in environmental compartments and inside biomass, there are more possible pathways in biochemical transformations. Nevertheless there are substances which escape biochemical transformation; in addition resorption by organisms may be limited. Hence, biochemical transformations need not be the dominant ones in an environmental system, competing against hydrolysis, photolysis or redox processes. Typical kinds of biotransformations include:

- Oxidation, particularly hydroxylation;
- Hydrolysis;
- Conjugation with polar anions or organic molecules (glycine, sugars, sugar acids, etc.).

In vertebrates these are mainly accomplished in the liver and serve to enhance water solubility. As a result, they are back-extracted into the intestine (guts) to facilitate renal and/or fecal removals; for example, while simple esters such as ethyl acetate are just poorly miscible with water, all the oxidation (ethyl glycolate) and hydrolytic products (ethanol and acetic acid, respectively) are readily miscible with water. When hydroxylated compounds like alcohols or phenols are produced from alkanes, alkylbenzenes or benzenoid aromatics by peroxidases, water solubility increases once again, and finally an entire hydrophilic side chain can be introduced by conjugation.

1.3.4

Reactions and Effects

An effect is the (every) kind of influence exerted by a substance or process onto some system which changes the state of the latter. In chemical effects it is hard(-ly meaningful) to distinguish between an effector substance and processes induced by its presence: a substance gets into the system, reacts or catalyzes with some other component(s) there and produces some by-product which either causes an effect or the production of which is the very effect. This general statement holds for systems of arbitrary chemical and structural levels of complexity. With living beings being chemical systems also, biochemical effects cannot be distinguished effectively from the “purely chemical” actions of intruding chemicals.

Dissolution of polymers by acids or bases is nothing but etching injury of biological matter, while precipitation of Ca salts of certain organic acids is the reason for the development of in-organ stones or gout (if the precipitated salts accumulate within joints). Gout can likewise be caused by suppressing xanthin oxidase (a Mo-dependent enzyme) activity by, for example, diclofenac in vultures, fishes (Section 4.3.2).

Besides, biorelated chemical actions include changing solubility relationships, causing an attack on lipid bilayers in cell membranes by organic solvents, or the formation of addition compounds like gas hydrates (narcotic effects of gases including N₂ and heavy noble gases) or quinhydrone (phenol toxicity) – neither of which is considered a “genuine” chemical reaction (cf. textbooks on noble gas compounds published before 1962).

All these correspond to biological action modes: attack onto cell membranes by solvents will bring about uncontrolled – or blocked – passage of ions causing severe neurological effects, while the formation of addition compounds by nonpolar reagents causes narcosis.⁶⁰ In addition there are yet more kinds and sites of action and effects: membranes give structure and divide compartments to and inside biological systems, have to be penetrated and passed by either diffusion or active transport during metabolism. Metabolism in turn spells ongoing chemical reactions which consume and produce substances on one side of a membrane anyhow; hence “simple” chemical transformations and effects from their products are superposed and modulated by reaction–diffusion coupling. In

60) The formation of gas hydrates (see also Figure 4.67) and similar addition or intercalation compounds (also in the synaptic gap, altering its width and hence lag times and acceptable excitation frequency) causes narcosis by the inhalation of narcotic agents like CHCl₃, diethyl ether, krypton (!) or cyclopropane (cf. gas hydrate sequestration of CO₂). If partial pressure is increased (e.g., 1.5 bar

with Ar, >3.5 bar with N₂), nitrogen, argon and so on exhibit narcotic effects also which limits their application in diving, with the high pressure nervous syndrome caused by rapidly enforced gas dissolution in tissues (by descending rapidly, say to 300 m within 10 min in a reported case) seizures, which sometimes kill directly rather than by secondary drowning.

corresponding reaction–diffusion systems there often will be chemical shaping of an environment, for example, by chemical waves (reaction wavefronts) which thus are also observed in biology, for example, Ca^{2+} ions during cell budding are obviously sensitive toward both excitation and changes in diffusion coefficient at the membrane. The membrane and its behavior can even be “manipulated” by surficial adsorption of ions and (non-reactive, see above) gases. This brings about another mechanism for action of compounds besides “directly chemical” ones, which would entail (possibly catalytic) change of substances or solution destruction of existing structures. The threshold for such indirect effects is much smaller than with chemical interferences.

Many substances get into organisms, some of them going to be enriched, deposited over long periods of time (PCBs in fatty tissues, heavy metals in either bones or kidneys) or to undergo chemical modification, that is, partially metabolized. Some of these metabolites will cause biochemical effects of their own, for example, PAH (ep)oxidation products are epoxides (benzoxiranes) and are capable of adding to nucleic acids by opening the three-membered ring, thus becoming mutagenic and much more toxic than the original compound. Effects from this or similar transformations can be systemic or just hit certain organs of one or several species.⁶¹⁾ In quite different organisms, the effects can be very similar, for example, Pb^{2+} inhibiting Zn-dependent enzymes are involved in prophyrin biosynthesis (see above, the effect being common to animals, plants, fungi and many kinds of bacteria altogether). Likewise 4,4'-bipyridinium salts like Paraquat interfere in both animals and plants with electron transfer in the respiratory chain because the $(\text{R}_{(\text{N})2}\text{bipy})^{2+/+}$ redox potential⁶²⁾ is between those of the respiratory chain quinones, causing oxidative decoupling of phosphorylation. But they can also vastly differ by interacting with certain items (enzymes, etc.) within grossly unlike metabolic networks; examples include the high toxicities of both Cu and La toward algae (and certain moulds) but not higher green plants or that of Ag against most bac-

61) Some examples: Whereas Be^{2+} , dioxines and also 2,2'-dichlorodiethyl ether are demonstrated to be carcinogenic in the guinea pig, the latter compound now is considered not to provoke cancer in humans. In animal experiments, teratogenic effects of angiogenesis inhibitor thalidomide are small but proved catastrophic in human embryos, while action as an angiogenesis inhibitor additionally allows for its use as a cytostatic agent also (in [non-pregnant!] humans).

62) Bipyridinium salts are N-alkylated pyridines which are linked back-to-back to each other, producing a dication, that is, 4,4'-diaz analogs of biphenyls or flourenes of general formula $(\text{R}_{(\text{N})2}\text{bipy})^{2+}$. Unlike simple pyridinium salts (including vitamin B_6) which take up a pair of electrons

reversibly, but similar to C-homocyclic polycyclic aromatics (PAHs), uptake of a single electron here to yield $(\text{R}_{(\text{N})2}\text{bipy})^+$ is also possible, producing a stable free radical which is considerably stabilized with respect to PAHs as the charge of the additional electron is “compensated” by two positive charges. Accordingly the redox potential is higher, and so much higher than in PAHs (there $\epsilon_{\text{PAH}/\text{PAH}^{\cdot-}} \approx -1.6\text{V}$) that paraquat and its derivatives do interfere with metabolic redox reactions which take place at quinones, jeopardizing (oxidatively uncoupling) ATP synthesis. The same toxic mechanism is seen with other aromatics strongly stabilizing negative charges, like 2,4-dinitrophenolate. The reversible 1e-transfer at paraquat sometimes is used as an electron relay in photoelectrochemistry.

teria. Neither silver nor rare earth elements (other than Tb) are significantly toxic against vertebrates.

Chemical reactions and biological effects can combine to produce ecosystems effects if different organisms as well as abiotic factors get involved, causing havoc often even if growth and reproduction of certain organisms at the basis of the trophic pyramid appear to benefit (eutrophication of lakes). Effects in environmental chemistry can, moreover, cause biological damages if they change the radiative spectra reaching Earth ("ozone hole", now going to diminish): although there are some 20–40 km of vertical distance between the region of corresponding chemical reactions (HalO_x , NO_x and HO_x cycles of photoinduced catalytic ozone destruction) the UV radiation which now comes to the surface not only more but to somewhat shorter wavelengths, is capable of causing damage in all skin, eyes (cataract), and vegetation. The toxicological effects which are to be discussed now depend on direct rather than spatially remote interactions between some reagent and the metabolism of some test organism⁶³ it interferes with.

1.3.5

Examples of Lipophilic Behavior, Accumulation and Toxicity: Kinds and Reasons of Effects Caused by Organotin Compounds

There is a really long history of attempts to correlate chemical structures or physicochemical parameters⁶⁴ to toxicity data or other dimensions of biological activities of substances, starting much earlier than corresponding work on (substituent effects in) chemical kinetics by Hammett (1973). The theoretical precondition for deriving such data was the theory of molecular structure (entities which exist in 3-D space, joined by chemical bonds between atoms), designed in the 1860s, which additionally, besides such spatial structures, postulated some relationship between these structural motifs and chemical reactivity.

As soon as one tries to describe such relationships by numerical parameters one ends up with a description which contains some kind of quantitative structure–activity relationship (QSAR) statements, the oldest corresponding approach dating back to this very time (Crum Brown and Fraser, 1868). Although comparative studies (comparative among chemical elements, not different animals or plants) date back at least to 1825 (Gmelin, on dogs), the periodic system of elements

63) Test organism here does not necessarily correspond to the whole-organism test, toxicological laboratory experiments or even active biomonitoring (see also Chapter 4.1.1.2, Definitions) but it simply denotes that effects are studied on a certain, given species or cell lines derived from it.

64) Typical quantitative structure–activity relationship (QSAR) descriptors include substituent constants which refer to changes of reactivity (in kinetic terms) by introducing some peripheral functional

group to a standard reactant system, for example, an arene (Hammett, 1973; Exner, 1972) or an alkene (Taft) while topological indices are focused with spatial arrangement of atoms in a molecule (including Hückel and HMO (Hückel molecular orbital) MO theories), or correlations which implicitly deal with HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital) energies, for example, by using redox potentials or spectroscopic properties.

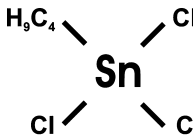
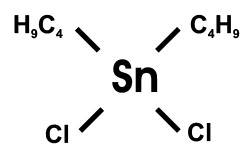
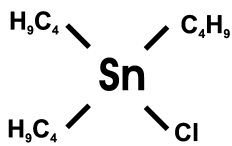
<p style="text-align: center;">inorganic tin</p> <p style="text-align: center;">Sn</p> <p>LD 50: ?</p>	<p style="text-align: center;">MBT = monobutyltin</p> <div style="text-align: center;">  </div> <p>LD 50: 2140 mg/kg BW</p>
<p>LD 50: 1360 mg/kgBW</p> <div style="text-align: center;">  </div> <p>DBT = dibutyltin</p>	<p>LD 50: 70 mg/kgBW</p> <div style="text-align: center;">  </div> <p>TBT = tributyltin</p>

Figure 1.7 A comparison of toxicity data for inorganic and butylated tin compounds in rat (Oehlmann and Markert, 1997). BW: body weight.

(Mendeleev and Meyer, in 1869) was required for any systematic treatment. Some time later the term “heavy metals”, now considered by many to be meaningless in toxicological terms, was introduced in 1904 for this very purpose. Soon after, the redox series of chemical elements was linked to their toxicity, an idea which was recently revived by Lewis *et al.* (1999). There are very sound and illustrative treatises on QSAR approaches which make use of either “purely” empirically chemical data or terms from quantum chemistry, topology and the like (see Schüürmann and Marsmann, 1991; Schüürmann and Segner, 1994; or sofar as PAHs are concerned, see Balasubramian, 1994; Borosky, 1999).

In species which are centered on tetravalent tin, if the chloroligands are replaced one by one by *n*-butyl groups, the lipophilicity and log k_{ow} will obviously increase considerably, accompanied by a tremendous increase in neurotoxicity and the propensity to accumulate⁶⁵⁾ along the trophic chain (Figure 1.7). Certain marine mollusks (snails) experience hormone-analogous androgen activities of R_3Sn^+ (tri-alkyl tin cation) ions, causing genital malformations (Oehlmann *et al.*, 1996). By

65) In certain cases, reaction between cobalamine (aquaform of vitamin B12) cobalt centers and alkylated metal or semi-metal compounds are reversible,

stripping alkyl groups from the latter rather than just producing biomethylation by methylcobalamine, but this does not occur with tin.

some QSAR approach, the effects of this stepwise replacement of Cl by $n\text{-C}_4\text{H}_9$, which concern the reactivity toward certain functional groups—including hormone receptors in organisms—can be taken in quantitative (QSAR!) terms. Moreover, while $\text{Sn}^{\text{IV}}\text{-Cl}$ bonds undergo ready hydrolysis (SnCl_4 is a volatile liquid “fuming” with HCl cleavage in moist air—*spiritus fumans Libavii*, after its sixteenth-century discoverer Andreas Libavius), Sn-C bonds are much more stable, but attacking sulfur centers to become irreversibly bound to proteins.⁶⁶ In 2004, the use of tributyltin paint additives for ships [hitherto used to preclude the attachment of algae and the larvae of sessile animals (mussels, barnacles, corals, sponges) on vessels, which increased their water drag] was banned for ships of >25 m total length. Besides this, triorganotin compounds were used in organic chemistry ($\text{Bu}_3\text{Sn-H}$ as H atom radical source, e.g., to start polymerization) and even, in the direct vicinity of human skins and bodies, for the disinfectant treatment of textiles!

1.3.6

The Term “Heavy Metals”⁶⁷ and Its (Purported) Chemical and Toxicological Ramifications

Whereas covariances between the (metal/elemental) density and the toxicity of chemical elements were noted as early as 1904, the relationship thus suggested was recently dismissed as a “non-descript term” (Nieboer and Richardson, 1980) even though it became really popular even in commonplace use of language. Since cation formation can cause substantial changes in atomic/ionic radii, solid-state properties of elements are unlikely to be related directly to chemistry. However, toxicity was observed to increase (often) with the oxidizing properties of a metal ion, like with Ag^+ , Hg^{2+} , Tl^{3+} , Au^{3+} or Pd^{2+} , or among the different oxidation states of vanadium, but the far less oxidizing uranyl dications are also highly (chemo-) toxic. So there should be a relationship with electron affinities in both atomic and ionic states which partly is due to the relativistic contraction of orbitals. This both increases electron affinity, and thus redox potentials, and reduces atomic radii, producing higher elemental densities of sometimes $>20\text{ g/cm}^3$. In addition, affinity to sulfur binding sites (Shaw, 1961), including the capability to cleave disulfide bridges in proteins by oxidative insertion (Hg_2^{2+} , Au^+ , Pt^{2+}), has a role in this “heavy-metal effect”. Toxicological correlations between oxidation potential and, for example, its (oral) toxicity toward *Rattus norvegicus* (Lewis *et al.*, 1999) does imply some assumption on biochemistry in the target organs, namely what will happen to the oxidation state and binding form (speciation) of an element in the body. If one cannot define the oxidation state and binding form (speciation) of an element in the body, no oxidation state of a given xenobiotic can be identified (notwithstanding problems of redox and complexation kinetics) and there is no

66) Polyalkyl tin or -lead ions are poor acceptors in coordination chemistry, producing feeble bonds to halides, oxospecies or thiolates, whereas neutral ligands hardly attach at all.

67) For the definition of the term “heavy metal” please have a look on footnote 35.

way to define any redox potential; thus, the above correlation then cannot be established at all.

Though not really arbitrary, oxidation potentials have but limited validity in bioinorganic chemistry as the actual array and concentration of active ligands in biomass is poorly known (even though a parameter for average coordination behavior of biomass samples can be deduced from biofractionation properties; Fränzle, 2010), putting some doubt on toxicological conclusions linked to the above oxidation potentials. However, as noted before, the attack of certain heavy metal ions in lower oxidation states [in fact, all the heaviest non-radioactive elements of all ($Z = 75-83$) except for Tl and Bi, which are too hard to oxidize to react with perchalkogene moieties] is typical, observed with those metals almost in general and with many organometal compounds: cleavage of disulfides by oxidative insertion which affords thiolatocomplexes of Hg(II), Au(III), Pt(IV) and so on. As these disulfide linkages are ubiquitous in biochemistry except perhaps for some organisms dwelling in extremely reducing environments, such as clostridia or methanogenes, these elements are strongly toxic regardless of taxa or even kingdoms of life; the respective heavy metals are likely to inhibit most of those transformations which are accomplished in environmental engineering making use of organisms. Sewage treatment plants may succumb if there are too much heavy metal in inflow water, and the final limit of phytoremediation is heavy-metal toxicity. There are some plants which tolerate substantial levels (e.g., ferns like *Diopteris vittata* or various *Thlaspi* weeds) but they are very small, their roots only capable of cleaning the uppermost few centimeters, and their growth is slow; hence, phytoremediation is surfacial in either sense of this word and going to take a very long time. Nowadays relativistic numeric quantum chemistry is advanced to such a level (Pyykkö, 2000) that this insertion process (Sperling and Steinberg, 1974) and other typical features of elements with $Z > 70$ are accessible to theoretical treatment, besides experimental work.

Given this, why should there be any relationship between metal density and toxicological features of its chemical properties? Empirically, all metals of $Z < 23$ are light metals ($\rho \leq 6 \text{ g/cm}^3$) and in addition display class A behavior as defined by Ahrland, Chatt, and Davies (1958). For $Z > 50$, all but Eu are heavy metals in the above definition, moreover, class B behavior is quite general except for REEs (Nieboer and Richardson, 1980). The reason is as follows (Fränzle and Fränzle, 2002):

Atomic radii do not significantly increase from Li or Be (the lightest metals at $Z = 3$ and 4, respectively) up to the said $Z \approx 80$ heavy elements owing to relativistic orbital contraction (the binding energies, and thus mass gains, of the innermost electrons then are about 20% of their rest masses, making these orbitals shrink by >15%); hence densities should increase almost like atomic masses by 20–30 times, and they actually do so [cf. Li ($\rho \approx 0.53 \text{ g/cm}^3$) and Pb (11.3), or even $Z = 74-79$ ($\rho = 19-22.6 \text{ g/cm}^3$)]. Now, at $Z > 70$ there are lots of electrons rather closely packed which thus strongly interact regardless of their allocation to correspondingly many orbitals (spin-orbit coupling also is a result of special relativity). This large number of similar orbitals at higher fundamental quantum

numbers permits electrons to escape correlation to some extent, making use of another orbital very similar or even identical in energy. Accordingly, polarization readily occurs in both metal and ionic states, and the ions become “soft” (class B) to prefer the binding of donors like iodide, phosphines or selenium compounds. With both mass and charge of atomic nuclei being large, the attraction of the outermost electrons becomes strong. Hence, for $Z > 74$ these are fairly hardly oxidizable (except of Tl), often even noble metals, while their ions can be readily deformed and thus polarized and hence they readily bind to heavy chalcogens or pnictogens (S, Se, As, etc.).

1.4

How to Determine Environmental Pollution

1.4.1

From Methods of Trace Analysis up to Understanding the Underlying Processes

Analytical data “as such” do just provide information on concentration levels and distributions of elements and compounds which are measured. If we deal with trophic chains or networks, distributions among food and certain organs of the body or the relationship between soil and (given part of higher) plant concentrations, the values so obtained are obviously linked to each other. This may correspond—or serve to check the latter—with ideas on which processes are involved in transport between the pairs of compartments or element matrices which are considered. Such processes include diffusion, with or without the formation of complexes, in active transport in organisms, which is accomplished using and consuming ATP, and “leaching” of soil solids by organic acids which behave as ligands and are delivered into the rhizosphere of both trees and grasses. Models which account for these transport processes necessarily draw upon “chemical” concepts and terms for description purposes. Now we must turn to the purposes of environmental sciences and also applications in environmental engineering which are the factors and biogeochemical features to control and direct the fluxes of both elements and compounds through some trophic chain or—spatially—across an ecotone, regardless whether this transport is “wanted” (biofortification, bioremediation) or rather causes problems and hazards. Obviously, this is related to running plants like sewage treatment plants.

Because chemical compounds can bear a number of different functional groups which are themselves comparable to those of the more abundant chemical elements and in addition can almost freely combine⁶⁸⁾ most of these functional groups—two or more different of them—in a single molecule, their chances to undergo quite diverse chemical reactions (some of which will spell cleavage of pollutants) are far larger than those of inorganic ions, including oxoanions of both

68) Except for spatially close pairs of functional groups which interact inside or among (a) molecule(s) to yield either polymers (polyamides including peptides, polyesters) or salts (including cyclic sulfonium or ammonium [aziridinium] salts) readily.

non-metals (Si, N,P, As, heavy halogens) and metals like V, Cr, Mo and so on. Thus a detection and quantification of elements by trace analysis, coupled to a determination of environmental parameters pertinent to chemical potentials (pH, Eh) allows for a rough estimate of toxicological conditions only, and the same holds for the range of biochemical transformations (including biomethylation) then possible, whereas the stabilities of functional groups like aldehyde or nitro moieties may also be limited. For very nonpolar compounds or metabolites, bioaccumulation can occur (which is very rare in inorganic species), increasing biological effects regardless of whether these compounds remain in their original states and adhere to lipophilic receptor sites much as, for example, steroids would do or cause narcotic behavior or become transformed into other compounds or ions which then can react with corresponding receptors and other biochemical items, sometimes even irreversibly. While toxicity values do not differ vastly among the speciation forms of most metals, matters are quite different concerning non-metals such as F, Cl, P, N, or As. Here pH and Eh really matter. If there is nonbiological enrichment owing to low volatility and/or strong adsorption (which also tends to increase with $\log k_{ow}$), these processes will amplify the effects of increased toxicities of certain speciation forms and bioaccumulation to cause grave adverse effects even though only a minute part of the said element (non-metal or Sn) is present or converted into such a form. Examples include dioxins formed both during forest wildfires and in waste incinerators, the photochemical formation of the former by UV excitation of PCBs and the halogenated phenylphenols formed thereof. Besides strongly increased toxicity, adverse properties might persist over generations:

- Not only dioxins but also otherwise harmless compounds like solvent dimethyl formamide (DMF) can be strongly teratogenic, causing congenital but not genetic malformations in embryos or fetuses, while in addition:
- The number and structural manifold of mutagenic agents⁶⁹⁾ is far larger among organics than in heavy-metal salts, with the effects of mutagenic agents persisting over many generations.

Both features co-act to further increase both the extent and the spatiotemporal range of implications and effects due to such compounds. Fortunately, this fatal cooperation is somewhat alleviated by organic substances being (usually) more readily degradable—and degradable in other, more diverse ways—than inorganic ones; however, they tend to accumulate in trophic chains. This increases the concentrations of ultratrace pollutants to such an extent that endocrinic disruptor effects on polar bears in the Arctic (Svalbard Island; Wiig *et al.*, 1998) and alligators in the south eastern United States (Guillette *et al.*, 2000) become obvious, as was the decline of large birds feeding on fishes, other birds or carcasses of dead

69) This statement mainly refers to humans and their kinds of exposition. Both other mammals, including rabbits to which Be salts or TCDD are acknowledged to be carcinogenic and newts which possess

these fantastic abilities to re-grow lost limbs completely but are the more sensitive to chemical perturbations which can have these repairment mechanisms run readily out of control.

mammals (see below). In former decades, the principal agent to blame for this was DDT, the endocrinic properties of which influenced Ca uptake into eggshells so much that the eggs still laid down could no longer be bred without destroying (squeezing) them, after DDT ($\log k_{ow} = 6.8$; Verschueren, 1983) had accumulated in the fat of fishes eaten by, for example, ospreys or white-bald eagles. These endocrinic effects tend to hit top-level consumers only, but even second-level consumers can suffer in certain situations also: like in humans, *Diclofenac* [3,5-dichloroanilinophenyl-2-acetic acid,⁷⁰ as the Na or $\text{NH}_2(\text{CH}_3)_2^+$ salt] was until recently commonly used in veterinary medicine as an analgesic and anti-inflammation agent. However, there was a real collapse in vulture populations in India and Pakistan which ate the carcasses of beef or goats treated like that. As a result, carcasses lie around much longer than elsewhere in these hot climates, spelling increased risk of epidemics. In any case, such an almost complete removal of top-level consumers—be it by excessive hunting or chemical impacts which hurt reproduction—is going to cause grave effects on an ecosystems all the way down to producers.

The processes and effects of organics (not just phenols which directly resemble estrogens in structure motifs) are thus going to hit—though indirectly—more and more different species in some ecosystem than “inorganic pollutants” (would) do, owing to the propensity for bioaccumulation. If the latter occurs to such an extent that toxic, reproduction-toxic or other endocrinic effects become considerable next to the top of local trophic chains, the derivation (in fact, devouring) from biomass, components thereof and the population dynamics are influenced in all the lower trophic levels also. Ecological stoichiometry studies did underline the effects of consumer-driven nutrient recycling (Vanni *et al.*, 2002; Elser and Urabe, 1999) that the (effective, average) length of trophic chains also is relevant for the distribution of bioaccumulating organic pollutants in the biota: once top-level consumer populations are destroyed in an ecosystem, the average lifespans of the lower-level consumers (or even plants) tend to increase which means that they will accumulate higher average levels of the said organic compounds. The problem also exists with inorganic toxic elements such as Cd, but at least these do not undergo biomagnifications via consumers. Heavy metals might cause problems though even if they are essential (excess Cu, Mn, V, or even Fe being considerably toxic) but the effect is not amplified via the trophic chain as these elements are not going to biomagnify—except perhaps for some which readily undergo biomethylation to form products stable enough to be handed up the trophic chain (As, Sb, Hg, possibly Bi and Pb⁷¹).

70) While just a few species of vultures are vulnerable to this effect, which brings about kidney failure and muscular inactivation, none of them are new world vultures (of which condors are more closely related to storks rather than old world vultures). 3,5-Dichloroanilinophenyl-2-acetic acid also readily passes through sewage treatment systems without any

degradation and just limited adsorption. However, it can readily be degraded by sensitized photochemistry (Fränze *et al.*, 2010; Chapter 4.3.2).

71) For the neutral methyls (as far as is known, other alkyls or aryls are formed only with As and Hg) $\log k_{ow} < 5$. Accordingly, biomagnification is feasible only.

To put it into a nutshell, it is essential to supplement trace element analysis by speciation analysis to get any idea, let alone prediction on processes and consequences linked to the presence of certain elements in apparently unusual concentrations. Speciation analysis is already required to understand the processes as such, to find out whether precipitation, biomethylation and adsorption to particulate organic matter or to sediments occur at all. These processes of course are controlled by solubility and the well-known effect of $\log k_{ow}$ on adsorption also.

Even then, demonstration of causal relationships remains an issue, because correlations among certain factors can never give proof of the ideas on models or on causality at all, regardless of how large the correlation coefficients or levels of significance may become. Popper's venerable principle that the falsification of a working hypothesis must be (i) both possible at all and (ii) feasible in an operational manner cannot be readily applied to macrosystems in environmental sciences. These macrosystems which often are investigated in environmental sciences possess highly sophisticated feedback structures which can bring about non-linear or even oscillatory behavior and their dynamic complexity cannot be grasped simply, making it very difficult to test hypotheses on their modes of action in a convincing manner. But moreover, there are severe ethical concerns in doing corresponding experiments, given that many of the effects on both structures and functions of ecosystems would be irreversible. Then reasonable concerns that problems arise from ongoing anthropogenic changes should urge us to correct mis-developments before the full-scale damage has been done and becomes irreversible. Examples of such anticipation of severe problems and corresponding measures already mentioned in this volume include the greenhouse effect and the other CFC-related issue, ozone destruction.

Nevertheless it must be maintained that hypotheses concerning causes, effects and modes of effects in environmental sciences must be formulated according to the same strict criteria as elsewhere in the exact sciences, that is, both conform to the laws of nature, including the principle of causality and being liable to experimental (or observatory⁷²⁾ falsification. Later Nobel laureates Svante Arrhenius,⁷³⁾

72) It is not just a drawback of environmental sciences that: (i) certain clarifying experiments cannot (ought not) be done for ethical reasons (the same with medicine!!) and (ii) observation and numerical simulation of natural processes must replace an actual experiment (cf. astronomy: stars are not directly accessible, let alone subject to experimental manipulations, and even testing thermonuclear warheads would not correspond to or be suited to simulate any phase of evolution of a star . . .). Accordingly, environmental sciences cannot be dismissed as "soft" sciences as long as Popperian criteria are fulfilled by acting like in other areas of science

(medicine, astronomy) to gain evidence in the sense of empirically robust knowledge hard and unlikely to falsify any time later.

73) Note that his seminal work on the greenhouse effect (1896) had no relationship to those branches of physical chemistry the development of which would Arrhenius earn a Nobel seven years later: this was on the formation of ions in conventional chemical systems, simply by the dissolution of salts or acids or bases, and these ions being the reason for electrical conduction and the feasibility of electrochemistry in such (aqueous, alcoholic, etc.) media rather than in salt melts only.

Sherwood Rowland and Mario Molina (to name but a few) were motivated by such thinking to issue stern warnings based on chemical and spectroscopic reasoning much before that level of evidence on the corresponding topics could be gained which shapes contemporary discussions and measures.

1.4.1.1 Inorganic and Organic Compounds

Environmental sanitation cannot and should not be started unless one has a sound idea of the situation around. For this purpose, concentrations of chemical compounds, all “autochthonous”, biogenic and anthropogenic/xenobiotic, must be determined by some analytical procedures and, given that toxicities (especially of non-metal compounds) sensitively depend on the mode of binding, this must be done in a couple of different ways. There are more general ways (technical methods) of analysis which are restricted to the presence of elements only, disregarding (or destroying during sample preparation, if there is any⁷⁴) any information on chemical bonds these elements are/were integrated in. As chemical elements are generally considered to be “inorganic” items (a relic term from the times of vitalist views disregarding that biotic and non-biogenic samples, molecules, etc. in fact consist of the same set of chemical elements), the elementary analysis is called inorganic analysis. Moreover, the detection and determination methods in inorganic analysis usually depend on atomic or even nuclear [instrumental neutron activation analysis (INAA), mass spectroscopy, Mössbauer spectroscopy] properties while organic analysis (and speciation, see below) deals with and makes use of the properties of complete molecules or molecular ions (even though these molecules are not always unchanged after the analysis).

There are some kinds of analysis which can be done on the raw sample (just dried) but which do not afford information on binding modes or oxidation states, except for Mössbauer spectroscopy. These are called direct methods (direct because chemical sample preparation is avoided) and include neutron activation analysis (INAA), X-ray fluorescence spectroscopy (XFS, based on Moseley’s law), laser-pulse induced mass spectroscopy (MALDI-TOF) where some surface sample is evaporated and ionized by intense optical radiation, some varieties of graphite-furnace atomic absorption spectroscopy and the chemical information obtained by XFS when this kind of emission is excited by an electron beam during scanning electron microscopy.

So “inorganic” and “organic” analyses actually draw upon (and sample) different levels of matter organization hierarchy. Since valence electron binding energies are smaller than those of the innermost K shell (1s orbital) electrons or that among nucleons by many orders of magnitude, doing chemistry (if unwanted) is far easier

74) It is noteworthy that both the latter and MALDI-TOF can deal with effective sample sizes smaller than 1 μm , that is, in a range of <1 pg actual sample weight, allowing just a few thousand atoms of trace components to be detected. In crystals, XFS also provides some chemical information by the shift of onset

frequencies which is also obtained in Mössbauer spectroscopy but is there limited to a few elements and rather high concentration levels. MALDI-TOF might still provide certain chemical information if ions thus formed are not degraded to atomic ions but retain most or all of their chemical bonds.

to accomplish than nuclear transformations (even if the latter avoid electric repulsion when using neutrons⁷⁵). Organic analysis calls for more gentle methods of sample preparation and separation (extraction, chromatography) than inorganic analysis where often chemical binding patterns are deliberately destroyed to obtain some kind of sample (digested, dissolved, liquid, open to injection into some spectrometer) which is almost standardized with respect to the remaining components (e.g., an aqueous solution of nitrates or oxometallates of most different elements). In organic analysis, the molecules (including polyatomic ions from acetate or the like up to large anions) must be conserved while separating them first from their (usually biological, as there are few organics in minerals other than kerogen, lignite) matrix and then during separation of a organic analyte mixture. The former is usually accomplished by extracting the sample with some organic solvent(s) while the latter is done by some variety of chromatography, most commonly gas or liquid chromatography. After this step, the molecules may well be destroyed during identification unless the ultimate purpose is preparative natural product chemistry rather than analysis. This, for example, occurs in GC/MS where the molecules separated during gas chromatography are not retrieved but sent to a mass spectrometer which inevitably destroys them. Matters are different with high-pressure liquid chromatography (HPLC) where methods of identification leave molecules as they are (absorption spectroscopy or fluorescence spectroscopy).

Instrumental analysis:

1) *Inorganic compounds*

This is focussed on elements, destroying their original organic matrix to obtain solutions of element cations then to be analyzed without regards (which then are no longer available) to speciation forms.

2) *Organic compounds*

This deals with entire molecules (both neutral and charged) extracted from a matrix as they are. Here, speciation is an issue provided the combinations of chromatographic separation and identification allow one to grasp all the (major) speciation forms of the element. The identification is more critical than separation, especially if standards are lacking. This is fairly common in the diverse mixtures of compounds found both in biomass and in multiple- or diversely polluted sediments at sites, for example, carbochemistry includes the processing and application of coal tars. Nuclear magnetic resonance (NMR) and mass spectroscopy may be helpful in actually identifying the components of such mixtures.

- 75) This is also the message told by the history of sciences: whereas deliberate chemical reactions date back far before scripture was invented, the first nuclear transformation was accomplished only in 1919 by Rutherford [$^{14}\text{N} (\alpha, n) ^{17}\text{O}$] and radionuclides (unstable nuclei) were prepared only during the 1930s [first, $^{27}\text{Al} (\alpha, n) ^{30}\text{P}$] simply because much higher energies are required to start nuclear reactions [controlled (thermo-)nuclear fusion still is a challenge].

1.4.1.2 Speciation and Concentration

Except for the noble gases and alkali metal ions heavier than lithium, all chemical elements on Earth exist in gaseous or liquid phases in a larger or smaller number of different binding forms (i.e., notwithstanding their inclusion in most different solid phases like salts and minerals or primary forms created by radioactive decay in any environmental compartment or water). These so-called speciation forms include volatile or non-volatile halides, oxides, complexes of metals and often organic compounds many of which latter are produced by living organisms. What matters here is that often these different binding forms—speciation forms—vastly differ from each other and from the plain chemical element involved in terms of toxicity and also bioavailability. To understand and appreciate whether a given environmental concentration of, say, fluorine, arsenic or chromium actually poses a toxicological and thus environmental risk, one has to know about its kind of speciation or distribution among various speciation forms. Often already changes in ambient redox potentials will alter the situation gravely, perhaps more often for the worse than for the better, unless specific strategies are applied. Anyway, speciation must be determined and the array of methods applicable for this purpose is called speciation analysis.

Speciation covers various binding forms of the same element (except for elements existing in but one kind in the environment, e.g., cesium as aquated Cs^+ ion besides being part of certain minerals) and there commonly are several contributions of unlike compounds or ions to a total concentration in both the environmental compartments water (including raindrops), soil and in biomass. Concentration thus means a total concentration which is the sum of all these contributions, while there are individual concentrations for each of the species forms. Owing to different lipophilicity ($\log k_{ow}$, e.g., after biomethylation or complexation to compounds like phenols), volatility and propensity to form ions (sometimes also due to biomethylation, e.g., with As, Se, Sn^{76} , Hg) and hardly soluble salts, these speciation forms almost always display strongly differing distributions among the environmental compartments and biomass. In addition, their stabilities toward oxidants like O_2 , OH and NO_3 radicals also vary widely. For example, selenium can be readily volatilized from wet, reducing soils as dimethyl selenide but, once in the air, it will be attacked by OH radicals within minutes, and hence its average concentrations in air remain very small. While a total concentration can readily be determined after oxidizing digestion, speciation analysis brings about high challenges to separation techniques: (i) in organic analysis or ion chromatography to identify inorganic and simple organic ions, where the charges on the species to be separated will match or at least have the same sign, (ii) in speciation analysis we are often concerned with a mixture of all neutral, anionic and cationic entities of vastly different lipophilicity, polarity, solution behavior and so on. Hence, as a rule, it is not possible to get hold of all the speciation forms using a single kind of chromatography. There is an exception for heavy non-metals

76) While inorganic tin tends to hydrolyze into SnO_2 (cassiterite) rapidly, biomethylation is usually incomplete, producing organotin cations of different positive charges.

and some metals (Sn, organo-Pb, Bi, Hg) which can be volatilized by hydride reduction to afford volatile (alkyl- or aryl)hydridospecies.

The (concentration) terms ‰, ppm, ppb, ppt and ppq refer to different levels of dilution (10^{-3} , 10^{-6} , 10^{-9} , 10^{-12} and 10^{-15}), respectively. This may be depicted in transferring the problem to two dimensions (spatial areas): a stamp has an area of some 7 cm^2 . With the stamp lying somewhere on a colloquial desk ($\approx 1\text{ m}^2$), it covers about 1‰. If it lies down in your city house backyard garden (some 500 m^2), it will cover something like 1 ppm of the garden's surface. This same stamp in a small village site is equivalent to about 1 ppb. In a large city (some 700 km^2), like Hamburg or Birmingham, it corresponds to 1 ppt of surface area. Eventually, for the United Kingdom or Texas, it amounts to about 3 ppq of area. Figure 1.8 gives a visual example of the terms ‰, ‰, ppm, ppb and ppt after Markert (1996).

1.4.1.3 Quality Control of Analysis

In addition to the similar need for highest representative quality of the sample to be analyzed, most general rules and prerequisites of quality control in chemical analysis have to be taken into account (Markert, 1996; Markert *et al.*, 2003a,b). In the past 20 years a strict differentiation between the terms “precision” (reproducibility) and “accuracy” (the “true” value) has been established in chemical analytical research (Figure 1.20, Section 1.6.3). The practical application of this differentiation makes it possible to determine the “true” or real content of substance “X” in sample “Y”. The purpose of determining the precision of the data by repeatedly measuring the analytical signal is to track down and eliminate errors which might be generated, for example, by insufficient long-term stability of the measuring device (device-specific misadjustment). If the analytical procedures are not too complex, the precision will be 1–5%, and for most analytical problems this can be considered sufficiently exact. However, the mere fact that a signal is readily reproducible does not permit any statement about its accuracy. Even highly precise data can diverge greatly from the “true” (e.g., element) content of a sample. Correct analytical results can only be obtained if the entire analytical process is subjected to targeted quality control, where every result is checked for its precision and accuracy. Basically, two methods are now used to check the accuracy of analytical results: (i) use of standard reference materials (commercially available samples with a certified content of the compound to be measured and a matrix similar to the original samples to be measured in the laboratory) and (ii) use of independent analytical procedures.

A more difficult problem is that of accuracy during the sampling procedure, for at present we have no “certified reference system” as a calibrator for accuracy in representative sampling. As a rule, “polluted” and “unpolluted” systems will be compared, but there is no way to be sure of working accurately. The only possible strategy here is that of “independent methods”, when different research groups have the task of working in the same area with the same indicators, so that the data—obtained independently—can be compared. This is a very expensive method that can only be used in very special cases where method development is of general

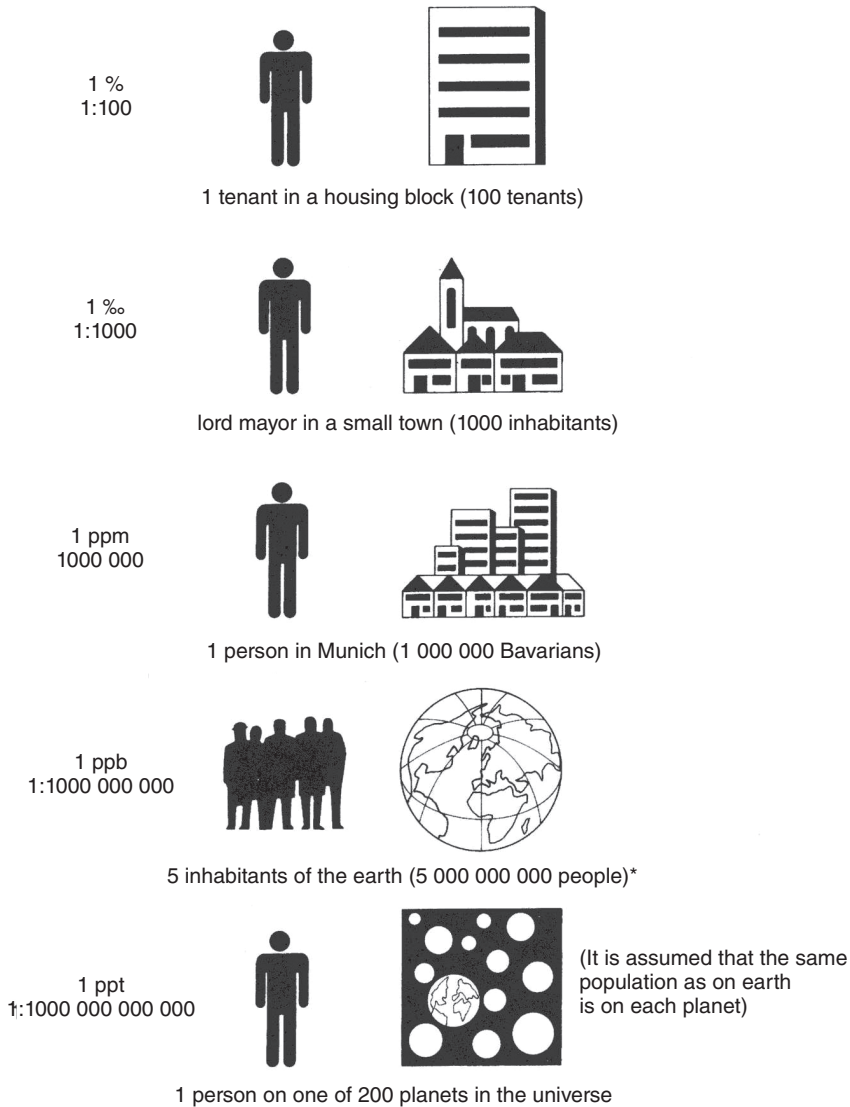


Figure 1.8 Illustration of the terms %, ‰, ppm, ppb and ppt. In extreme trace analysis the measuring range is often even lower by a factor of 10^3 , that is, in the ppq range (e.g., in the case of samples with a relatively low level

of dioxin and platinum metal pollution; Markert, 1996). *For sure, at the moment (2011) more than 7 000 000 000 people exist on earth.

concern, for example, for directives issued by the European Union (EU) or the United States.

1.4.1.4 Accreditation of Laboratories⁷⁷⁾

Accreditation now is an issue in many areas of society and its infrastructures. Certification by institutions within the EU is key to constructing, for example, the European Common Market. Certification is a means of politics of harmonization which aims at EU-wide legal harmonization by using guidelines to make legal norms as identical as possible. For this purpose, criteria of identical structures of laws and norms are supplemented by implementing and demanding identical procedures of certification. In doing so, European certification politics go beyond harmonization, because they also cover those areas which are voluntary and not covered by common legal norms (Berghaus, 1994). An end of European politics concerning certification and accreditation is to facilitate mutual acknowledgment of tests and certificates in order to avoid costly multiple tests of the same subject. This takes measures which create mutual confidence by the utmost degree of transparency (Berghaus, 1994).

Concerning universities, accreditation of studies apparently is an instrument of reliably maintaining and increasing the “quality performance” of certain studies, by means of an accreditation procedure which is done on a regular timescale and itself checked within reasonable periods of time.

However an example from analytical chemistry shows that undergoing a process of accreditation does not by itself provide some better or more accurate result. Figure 1.9 shows the outcome of a telling international experiment run by Paul de Bievre’s workgroup (with the EU-run “Institute for Reference Materials and Measurements” in Geel, Belgium).

This investigation was a round-robin analysis which belonged to IMEP-6, the International Measurement Evaluation Program “Trace elements in water”. The organizers sent identical samples of water (natural river water, the composition of which they knew exactly; Clear Creek, Colo., USA) to a total of 165 laboratories in 29 different States, asking them to determine 14 trace elements like lead (Pb) or cadmium (Cd). Groups of laboratories all over the world have taken part in such round-robin analyses for many years now, providing valuable information on the performance of certain analytical laboratories with respect to both accuracy and reproducibility of measured parameters. In addition, IMEP-6 generated information on accreditation, simply by asking the involved laboratories to state whether they had undergone accreditation, certification or other procedures designating them “officially acknowledged in analytical chemistry” (“AAA”-ranking) or not before taking part in IMEP-6.

Figure 1.9 shows the result for Pb level measurements in the water samples by either “non-accredited” (a) or “accredited” (b) laboratories: just a few among the non-accredited laboratories obtained the certified value of $0.133 \pm 0.003 \mu\text{mol/l Pb}^{2+}$ (value \pm confidence interval) but the “accredited” laboratories did not perform

77) According to Markert and Korschak (2003).

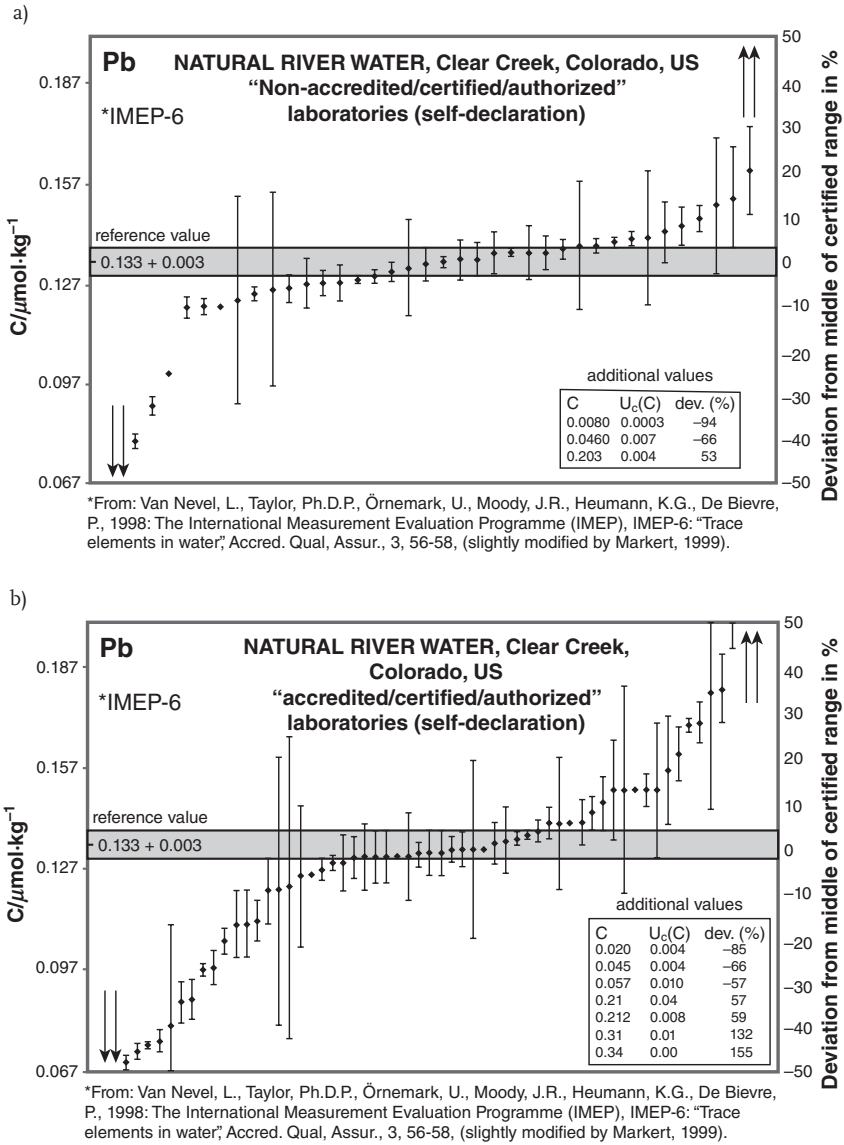


Figure 1.9 A comparison between quantitative measurements of Pb in “natural river water” (Clear Creek, Colo., USA) among “non-accredited” (a) and “accredited” (b) laboratories which took part in IMEP-6 comparative analysis (modified from Van Nevel *et al.*, 1998).

better (Figure 1.9b). The general result of IMEP-6 was that accreditation did not (positively) discern accredited versus non-accredited laboratories with respect to quality of results obtained by them, or, to put it frankly: “. . . there is little correlation between the self-assessment of the laboratories and reality . . .” (Van Nevel *et al.*, 1998). At least for this investigation prior accreditation of

laboratories did not improve accuracy of measured data and thus the quality of measurements.

1.4.2

Physical Methods in Chemical and Environmental Analysis, Modeling Ecosystems and the Role of Ecotoxicology in Integrative Environmental Sciences

Ever since people started to try to understand biological processes in quantitative terms of mass transport, transformation and accumulation, that is, like looking at chemical reactions, they obviously chose and employed chemical methods of analysis and “book keeping.” Probably the first to do this was Dutch chemist Jan van Helmont early in the seventeenth century. He noticed that a small seedling would be able to become a tree of 100 kg total weight or more within several years, taking water and the components of wood ash from the soil while carbon was apparently obtained from air somehow during photosynthesis. Around 1840, Liebig made use of elementary chemical analysis⁷⁸⁾ of plant biomass to translate these data on inorganic biochemistry (which had not yet been given this name) of biota into strategies to improve and sustain agricultural productivity. Liebig’s key results were the principle of minimum in theoretical and mineral fertilizer application in practical, applied terms. Much later, this body of knowledge was transferred from systems concocted by man to spontaneously arranging ecosystems, assaying nutrient cycles, generalized element cycles and limitation to ecosystems net productivity along that way of reasoning. Sometimes, corresponding experiments were done in open biocoenoses on an appreciable scale, for example, when trying to control and enhance CO₂ uptake by algae in the open ocean (Aumont and Bopp, 2006), fertilizing scores of square kilometers by Fe(II) additions. Given the scarcity of iron in the ocean, the idea was to increase photosynthetic productivity and have the algae escape C recycling by their sinking to sea bottom and becoming a (rather inactive) part of the sediment, but it turned out that most of them were eaten still in the photic zone, thus jeopardizing carbon sequestration.

Of course, similar experimental work was also done in systems which have a well-defined outer edge and limitation, like a couple of inter-connected small lakes in Canada. Besides measuring the pathways of various elements through these lakes and the local biota, the latter biota was arbitrarily changed in composition, length of trophic chains and so on by introducing novel consumers or else removing (catching, fishing almost) all of the creatures which represented certain trophic levels. It turned out that such complete removal of top-level consumers⁷⁹⁾ might seriously alter the aquatic chemistry of lakes and also seriously influence the ratios

78) Looking at the history of element discoveries, you will notice that this was about the earliest time such an approach could be done, given the fact that the most reactive of the major elements present in a plant than had just recently been identified and isolated. This holds for both essential

(K, Mg, Mn), sometimes essential (Si, Br) and non-essential (Al) elements likewise.

79) Keep in mind that these need not even be part of the in-lake biota but can also be adjacently living air-breathing vertebrates preying on fish or zooplankton, like bears, otters, ospreys or even flamingoes.

among species of lower trophic levels. Therefore, corresponding experiments are an ethical issue now also, but their role in the history of empirical ecology (and ecological stoichiometry) went far beyond learning with regard to the effects of unwanted or, to say the least, uncontrolled N or P inputs as the sense of the problems got sharper. This sense of the problems in turn did not just change their accepted and preferred choice of methods in experimental ecology but also had an impact on the expectations that society [in the USA, Canada and most parts of (western) Europe] would direct to the implications and importance of these—primarily chemical—kinds of works in environmental research.

1.4.2.1 Analytical Chemistry

“Purely” experimental manipulations in aquarium tanks, mesocosms like lysimeters or small ecosystems (like the above lakes) were augmented and partly replaced by investigations of ecosystems in their actual states, be they close to natural, significantly perturbed/polluted or even recently originating from anthropogenic activities, like lakes forming in quarries or open-mining pits or highly unstable man-made association of organisms in agricultural systems. During the past 50 years or so, sensitivities of analytical gear increased tremendously, with solid-state microelectronics allowing much work to be done on site rather than making all the analyses in the laboratory after removal of the samples and (all too often long-distance) transport. Thus many species, both inorganic and organic, could be determined down to the levels which are ubiquitous in the environment (for many trace elements, like rare earth elements, the actual levels in living organisms such as terrestrial green plants are still lower—nothing like bioaccumulation here!). During the twentieth century, several, now most important instruments, were developed for analytical purposes, like mass spectrometers (Aston, 1922), column chromatographs (Tswett, 1906) and, later, gas chromatographs (for historical beginnings and developments, see Martin, 1952), electrochemical analytical procedures, neutron activation analysis or X ray fluorescence spectroscopy.

These methods could then, additionally, be linked to each other, the results thus referred to as *hyphenated* methods, including most diverse ways of detecting organic compounds or metal ions after prior separation by some kind of chromatography. For example, it is most commonplace to attach a mass spectrometer to a gas chromatograph (GC/MS; Figure 1.10) for obtaining additional pieces of information which then allow (sometimes, at least) the identification of volatiles.

With analytical chemistry thus benefiting from technical progress and outright innovations, one now could ongoingly grasp the complexity of environmental processes and transformations (and the sizes and kinds of human interferences within those) in its “real” dimensions. Systems sciences added methods to deal with this complexity which had long been felt rather than seen by way of numerical simulation. Although electronic calculators (computers) were very helpful in this development, eventually allowing the running of ever more sophisticated models of in-system interactions on any PC available in laboratory or office, the mere fascination of “number-crunching” for purposes of outcome simulation (“change the start parameters a little bit once more and see what happens then”) often

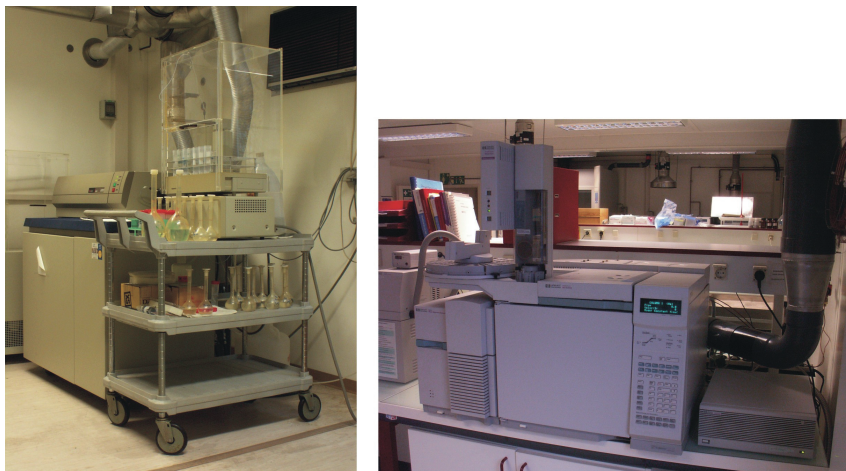


Figure 1.10 Some kinds of analytical commonplace in technical environmental chemistry. Left: A mass spectrometer in which the required atomic cations are produced in an electrically heated plasma torch (ICP/MS) which thus is meant to determine elemental

contents. Right: A gas chromatograph fitted with a mass spectrometer (GC/MS) designed to detect and quantify volatile (mostly but not necessarily organic) compounds (photos by Stefan Fränze).

tended and still tends to obscure reasoning in systems sciences to address causal relationships. Phenomenological reproduction of observed behavior is not the same as actually understanding it, but understanding is required in order to change the chain of events in those cases where pollution has to be tackled. However, numeric reproduction should not be considered a wrong approach either, since often there are no solutions for modeling equations whatsoever in terms of differential equations and thus one must resort to numerical simulation. The same holds if non-steady processes are to be described, say in combustion analysis inside engines which is mainly non-steady, including ignition and the explosion of gas/fuel/air mixtures, to be studied by spectroscopy (“glass-cylinder engines”; Winkelhofer and Fraidl, 1998) or—partly—by numerical simulation. The same holds that there is no alternative to numerical simulation for non-steady processes. Starting with a paper by Robert May from 1976, chaos theory got most popular even outside the scientific community although its beginnings are far older [Laplace around 1800 for celestial mechanics (Laplace, 1902), Poincare around 1900, Lorenz (1963) for the limitations of weather forecasting].

1.4.2.2 Geographical Information Systems

Geographical information systems (GIS) maps permit one to superpose different sets of space-related data in a manner which gives additional information on mutual dependences among different phenomena. Of course, ecological problems such as net productivity depending on either climate or the availability of certain nutrients can be tackled in this very manner, also. An early example of GIS applied

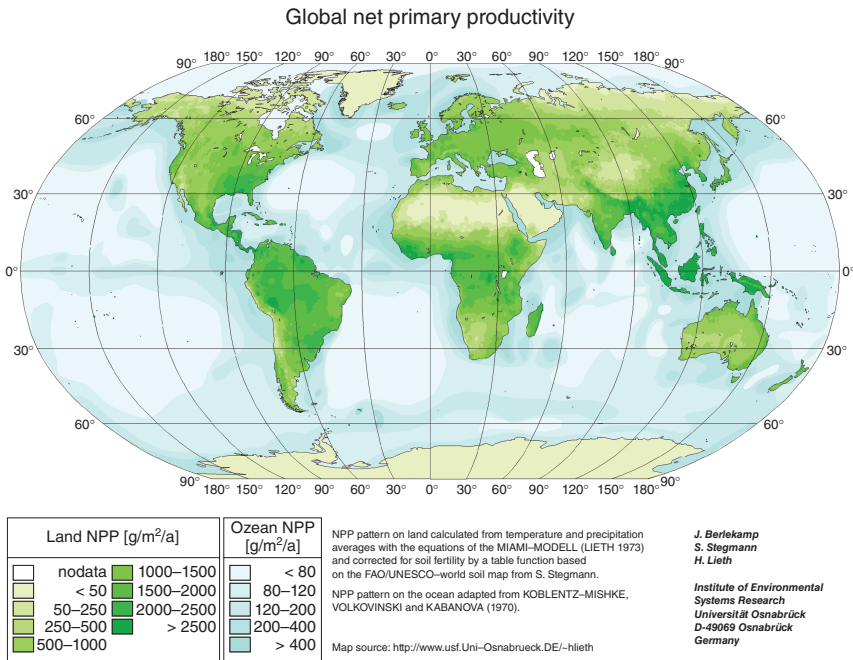


Figure 1.11 Rio Model 1995 (corrected for effects of soil fertility) for global net primary (photosynthetic) productivities. GIS/Arc Info Map, courtesy: Helmut Lieth, <http://www.usf.uni-osnabrueck.de/~hlieth>.

to global ecology was the net photosynthetic productivity maps by Lieth (1995, Figure 1.11). Here quite diverse (possible) effect causes, like climate (average temperature, solar photon flux rates), water availability (e.g., Sahara desert and tropical rainforests⁸⁰) on about the same geographical latitude) and certain nutrients in the ocean. This is relevant in everyday work rather than just to historians of science as these particular GIS maps contain some message on the chances to bind CO₂ by vegetation purposely grown in certain regions and thus also states of the world. This is significant given the Kyoto Protocol allows for validating—and trading—CO₂ cleavage activities linked to re-forestation of certain areas promoted or funded by others to “buy” emission certificates. Moreover some highly industrialized countries which are in an economic position to buy emission rights are not only densely populated but also distinguished by very low net photosynthetic productivities, including their marine surroundings if the countries are insulas or peninsulas. Examples include Korea (either part), the United Kingdom and the

80) As there is almost perfect nutrient recycling (plus some inputs by Saharan dust across the Atlantic Ocean), the Amazonian hylea is best suited to mislead people on its net productivity, which is

close to zero, rather like in the Sahara or Gobi deserts. You will soon notice this when you try to extract nutrients on a regular scale by doing agriculture there without recycling in the *terra preta* mode.

western parts of North America. Accordingly, these areas are going to be net producers of CO₂. Even though the situation is considerably better for the rest of Europe (outside UK), a mere 7–12% of carbon dioxide produced there can be reclaimed by its “own” vegetation at all.

GIS maps are also very useful, for example, in moss-monitoring campaigns (Figure 4.7, Section 4.1.15).

1.4.2.3 Biotest—Biological and Ecotoxicological Implications

With physicochemical parameters such as pH, concentrations of certain (other) compounds and UV luminosity being measured in some environmental compartment, the actual biological and ecotoxicological implications and a description of the drawbacks of chemical changes for living beings or entire ecosystems can only (at best) be inferred in an indirect way. This takes an extrapolation from what is known about optimal or marginal (respectively) living and reproduction conditions in terms of chemical effects thereon of certain species to the ecosystems metalevel. Of course, results thus obtained may be more or less clear or ambiguous; for example, the discussion on the reasons for forest dieback and the possible causal chains involved went on for more than 20 years. The reasoning which prompts and makes one design some biotests is quite different. One can, so to say, turn this approach upside down: some (a group of, for statistical reasons) test organism(s) can be brought to a polluted environmental site or brought into contact with some sample taken therefrom (e.g., exposing fishes, snails or zooplankton crustaceans like *Daphnia magna* to sediment samples⁸¹⁾) in order to evaluate physiological changes caused by this exposure, usually done over a defined period of time (say, 48 h or 30 days). Among the range of corresponding effects are:

- Rate (percentage) of test organisms to die within the given period of exposure time;
- Reproductive toxicity, including all budding rates of bacteria, sterility of metazoans, egg dieoff, embryo or hatchling deformations, miscarriage rates and deformations of genitalia caused by endocrinic activities of some compounds;
- In animals, changes of behavior [reaction time lags, aggression, speed of swimming, coordination in tricky environments (e.g., when balancing on some pole), changes of preferring dark or bright surroundings, reduced capability to cope with labyrinths or other difficult to grasp environments, etc.];
- Changes of skin color (bleaching, pathological pigmentation, short-term effects in animals which—like many fishes and cephalopods—use skin color or

81) This setup allows for testing limnetic (large river) sediments with marine organisms among which certain snails are most sensitive toward tributyl-tin endocrinic effects, or vice versa, exposing suitable freshwater organisms to seaside harbor sludges for evaluating the

toxicological properties of the latter. Likewise terrestrial sediments or mineral/ore/mining residue samples can be contacted with either freshwater- or seawater-dwelling test organisms (e.g., Matthiessen and Gibbs (1998), Leung *et al.* [2004]).

pigment pattern changes as signals), damages inflicted on certain surface organs (leaf interface, skin), including tumorogenesis;

- Production of “marker” compounds for chemical stress, including induction of enzymes and protecting agents like metallothionein or ethoxyresorufin-O-deethylase (EROD), an enzyme from fish liver cells which is induced by the addition of pollutants like dioxins.

EROD induction has a peculiar advantage for the detection of chemical stress, being hardly suppressed itself by the action of xenobiotic compounds (Whyte *et al.*, 2000). Accordingly, EROD test sensitivity surpasses that of most toxicological standard test procedures.

Figure 1.12 gives an example for outlining a biotest which makes use of permanent swimming inhibition of water fleas (*Daphnia* spp.) with their being dead being taken as the measured criterion (first item in the above list). Notably, it is still obscure what is the causal relationship—biochemical, neurophysiological or other—between the damaging effect measured in the biotest and the kind of purported environmental burden. For example, an enzyme may be inhibited or else misactivated by some heavy metal ion⁸²⁾ or a carcinogenic agent. In addition, the less related the test organism and the measured parameter are to the manner in which the human metabolism works, then the transfer to humans (or a third taxonomic species) must be demonstrated much more stringently. The conditions in which test organisms can or must be kept will dictate some selection from the above list and a hierarchy of the possible effects of intoxication which might be observed (from minor changes of behavior to death, hatchling deformations or sterility). Rational reasons must be given for which effect is to be selected (see Schüürmann and Markert, 1998; Oehlmann and Markert, 1999).

Let us consider an example of most clever biomonitoring. Among the numerous weakly electrical fishes, mormyrids like *Mormyrops kannume* (elephant fish, called so for its mouth forming a kind of proboscis) produce electric signals which are small (peaking at a few volts at most) but repeat very frequently and stably as long as the fishes feel well. In polluted waters, both the frequency of repetition and the shape of a single pulse will alter. In some drinking water supply plants this was and still is used to control water quality levels. The particularly attractive feature of this biomonitoring approach is that such electrical signals are most suited to automated digital analysis, much better than, for example, changes of color, behavior,⁸³⁾ or reaction times. Mormyrids hardly, if at all (only certain species) reproduce

82) As noted elsewhere in this volume, replacing Zn by Co in zinc-“dependants” often renders them *more* active than before. However, Co²⁺ is considerably toxic while the required daily intake of a human is a few micrograms(!), just about 5% of this being vitamin B₁₂. Accordingly, the increased activity of “cobaltified” Zn enzymes will get coupled enzyme reaction out of their mutual balance of turnovers among coupled biochemical pathways;

hence some intermediates will pile up or get depleted.

83) Yet, average swimming speeds and changes thereof caused by the impact of chemicals (corresponding to both “panic”, trying to avoid the substance, and to partial inactivation) can be monitored by determining the position which aquatic animals maintain in a conical (rather than cylindrical) flow tube.

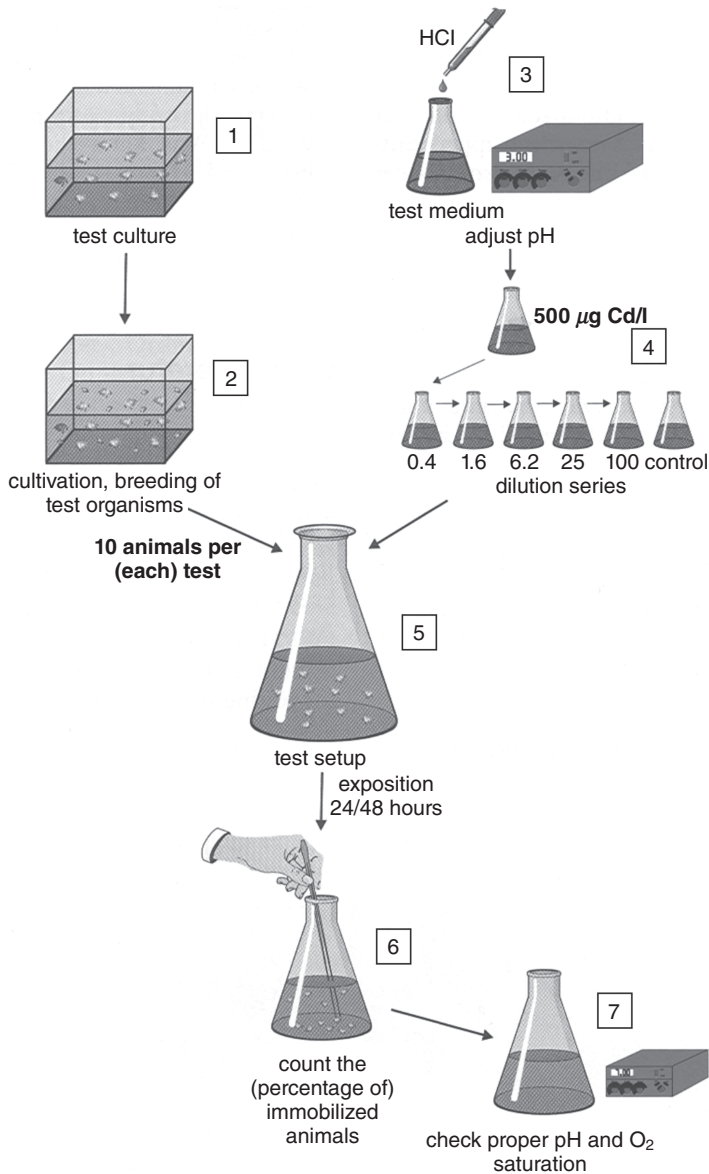


Figure 1.12 Schedule of tests on acute toxicity using *Daphnia magna* (see Fomin, Oehlmann, and Markert, 2003)). (1) Test culture, (2) breed the test organisms, (3) reducing pH of test medium to 2.5 to 3.0, (4) make a dilution series of Cd²⁺ salts: 0.4/1.6/6.2/25/100 µg Cd/l (four replicates

each), check pH again, (5) add test solution (10 young *Daphnia* per test setting), (6) count and remove those *daphnia* which became immobile (after 24 and 48 h), finally (7) check pH and oxygen content after termination of test.

in aquarium captivity, and hence studies based on reproduction toxicity are excluded [unlike with, e.g., fellow fishes *Poecilia reticulata* (guppy) and *Danio rerio* (zebra fish)]. While aquarium rearing must accordingly be considered somewhat stressful to mormyrids, the method of analyzing electric signals is considered reliable. Parameters other than reproduction toxicity which can be detected with mormyrids in aquaria of course include death and neurophysiological changes, the latter being better addressed by their intrinsic electrical activity than by changes of behavior. It must be pointed out however that, as these electrical signals are also involved in intraspecific communication, including mating behavior, fishes must be kept single for water quality surveillance to avoid perturbations by this kind of communication among the fishes (there are both solitary and swarm-forming species among mormyrids and their relatives). This is a telling example of the complexities involved in using animals, especially social animals, in biotests. Yet, among the >500 species so far employed in biotests (Markert *et al.*, 2003a,b), many are social animals with corresponding intraspecific communication avoiding perturbations of behavioral patterns, like rats or magpies (*Pica pica*).

Notably, there is no statement whatsoever associated to the effects used in biomonitoring as to the origins (causes) of the observed effects. It may be most difficult to identify the reasons of what is happening to plants, animals or bacteria under supervision. Notwithstanding this, a biotest still provides a “directly biological” statement on the possible effects of chemicals put into the environment. Accordingly, biotest and chemical analyses are a kind of complementary approaches to gain pieces of information on the “state of the environment”. In biomonitoring, being a quantitative approach, both are linked by using organisms to get information otherwise to be obtained from chemical analysis. Of course, scaling must be understood for the given system (Fränzle, 2010): you must know already how much lead is to be expected in leaves or fruits of some plant (species or cultivar XY) once a threshold level Z is surpassed in the underlying soil.

1.4.2.4 Locating Soil Pollution Sites by Geoelectric and Other Means

In both air and water environmental compartments, the principal components are fluid and mobile, causing a possible pollutant to be removed and distributed (usually rapidly) far around, starting from a given site of emission. Thus it can be detected far around by either analytical gear or biological effects after a short while. In soil, however, mobility is low, concealing pollutants often to the next vicinity of their origins, whereas heterogeneity of the soil system in chemical terms is thus conserved along all three dimensions. As, soil, moreover, is impossible to penetrate by light, precluding both photochemical alteration of components and optical spectroscopy, the detection (and remediation) of soil-borne pollutants must rely on something other than electromagnetic radiation next to visible wavelengths. For example, different kinds of pollutants may change certain soil properties in rather different ways. In turn, soil is highly variable with respect to its electrical and magnetic properties [consider inclusions such as Fe_3O_4 (magnetite) in B horizon iron pans or deeper layers], with biological attack on—especially

organic–soil pollutants in anaerobic conditions often vastly changing the corresponding parameters:

- When iron (Fe)-reducing bacteria (FRM) consume organics (and they will do so with quite a number of substrates, including mineral oil and benzenoid aromatics), the ambient paramagnetic Fe(III) is converted into the ferromagnetic materials maghemite $\text{Fe}_2\text{O}_3\text{-}\delta$ and eventually magnetite (Lovley *et al.*, 1987), producing local magnetic aberrations which can be detected from above the ground.
- Direct input of salts or acids will increase groundwater electric conductivity, and both might also originate from the onset of (now, aerobic or at least hydrolytic—there are plentiful exo- or postcellular hydrolytic enzymes in common soils) the degradation of halocarbons, esters and the like, besides direct input by spills.

As an example from archeology, earlier activity at a site can of course be pinpointed by finding [stone, metal (tools, weapons, coins), ceramic or wood] artifacts but likewise by alterations of the soil chemistry. Phosphate ions pile up there from either toilet sites or the remains of dead bodies in graves (even in the case of urn graves, as phosphates do not change during the incineration of a dead body; Zöllitz 1980a,b). Likewise there are other chemical signals persisting long after oil spills, digging away various poisonous wastes and so on. Besides affecting or even killing soil organisms, some of which actively try to escape such chemical challenges,⁸⁴⁾ the physicochemical features of soil will change also: salt spills increase electric conductivity, as does acid attack on clay minerals,⁸⁵⁾ and new interfaces in the soil created by chemical changes or an altered ground water level can be detected by seismic means (sound waves).

Soil bacteria and other organisms can “translate” chemical impacts into either magnetic signals—by producing partly reduced and thus ferromagnetic Fe oxides—or they can bring about changes of conductivity: producing organic acids will increase electrical conductivity, as will sulfide oxidation in mine tailing areas to yield sulfuric acid which is so good an electrolyte that it has now been used as

84) For example, earthworms. There is a test in ecotoxicology which just draws upon this behavior: in an octagonal basin separated into eight sections which have been filled with soil and “inoculated” with earthworms, one or several chambers are then treated by some chemical which possibly irritates or intoxicates the earthworms. If so, and if they do not die almost immediately (i.e., the applied dose simply was too large), they start creeping over the barriers into adjacent, untreated soil compartments to escape the nuisance. When doing so, they must come to the surface and can be observed directly or

surveyed by video camera. Escape behavior to evade chemical toxicity thus can even be put into comparative, semi-quantitative terms.

85) Whereas clays are pretty good electrical isolators even when rather wet, acidification below pH 4.2 will make them break apart chemically, leaving behind solid, still isolated SiO_2 (amorphous silica to sand) and rather mobile Al^{3+} and alkali cations which produce substantial conductivity moving around in ground water. Of course, the protons and acid anions (mainly NO_3^- and SO_4^{2-}) will also contribute to electrical conduction.

such in electrochemistry for more than 150 years continuously. In either case, perturbations which alter the speciation of elements (Fe, or S, respectively) by different redox potentials—pointing to admission of either organic reductants or of O₂ via cracks or in landfills and so on—cause readily detectable changes in the electric or magnetic or electromagnetic (georadar-based inductive signals) of soil, thus permitting one to look into it without digging or drilling for samples. Of course the methods are “blind” (insensitive) to pollutions which neither cause such changes chemically or biochemically or directly change conductivity (as buried metal scrap, in the most extreme case, would do). Isolating layers like clay do not pose very significant obstacles, however.

In addition, some animals use methods closely related to geoelectrics for both communication (area definition, mating) and spotting their prey which, in an aquatic environment, will differ from surrounding water, underneath sediment and so on, also by grossly different electrical conductivity. When at all active, potential prey will disclose its position by nerve and muscle electrical signals even when buried/hidden in the sediment. These electrical signals (peak voltage \approx 150 mV) are passively registered and used by, for example, hammerhead sharks, freshwater dolphins and platypuses; these animals will likewise reliably find a small battery dug into the sediment unless it is empty. Electric fishes such as mormyrids rather use active ranging, relying on their own emission of electrical impulses, like man does in remote sensing. These are weakly electric fishes incapable of using electric hits for attack or defense directly (3–5 V peak voltage at most).

So, like with the former example of iron (Fe)-reducing bacteria (FRM), the bacteria which use Fe³⁺ to oxidize organic nutrients, including petrochemical compounds, which include benzene, toluene, ethyl benzene and xylene(s) (BTEX) aromatic hydrocarbons (Lovley, 1991), subterranean metabolism will alter the physical properties of (either wet or dry) soil in a manner accessible to remote sensing. In addition, this process of iron reduction also influences retention and distribution of many other elements (Crowe *et al.*, 2006), for example, stopping the adsorption of As(V) to Fe oxide phases. Hence it becomes both feasible and urgent to detect pollution sites covered by soil without drilling literally millions of boreholes throughout the landscape—which no one could afford, let alone the risk of opening potential hazard sites which were hitherto contrived. So let us first consider geoelectric and geomagnetic methods of detecting differences between polluted sites and their surroundings. In fact, besides environmental surveillance these methods are also—and about as frequently—used to pinpoint other traces of former human activities, namely, in archeology.

The maximum in conductivity (minimum electrical resistance) which marks the very spot/region where a body was buried is due to the salts the body contained. After decomposition of the body, these salts in body liquids remained at the spot, increasing conductivity. The minima on either side are due to brick walls limiting the tomb, much like a sarcophagus (Matias *et al.*, 2006).

While this is small-scale, and thus appropriate for cases where the location of a soil pollution (e.g., an old landfill or spill site) is fairly well-known and just requires to get an idea of spatial limitations, the following example shows how large the

scale of such investigations can become: it is possible to “look” into soil, sediment and rock rubble some 100m deep while areas of dozens of hectares or even some km² can be screened. Here the task was to look for anomalous conductivity in a valley on a Greek island (Kefallonia) some 4.0km long and 1.5 km wide which now rises some 180m above the level of Ionian sea, which limits it both north- and southwards, linking a peninsula (Paliki) to most of Kefallonia somewhat east of here. The idea to be tested was that this valley was created only fairly recently by some landslide closing an isthmus between East Kefallonia and what (if true) had been an island of its own before (contributing another hypothesis to the ongoing controversy where to locate ancient “Ithaca”—not necessarily the island thus named today—as mentioned by Homer). If so, deep layers should be a “chaos” of intruding, highly conductive seawater and well-isolating large boulders one of which can still be seen hanging over a famous beach site and display high but heterogeneous electric conductivity. Notably, conductivity measurements were done by airborne electromagnetic (inductive) methods rather than boring poles into the site and apply voltage to them, much like magnetic anomalies like iron ore stockpiles are detected.

So investigations are feasible from decimeter to kilometer dimensions, looking deep into the ground. Even larger depths (>> 100m) and scales can be tackled by seismic rather than electrical, electromagnetic (“georadar”) or magnetic methods.

1.5 Biological System of the Elements

The Biological System of the Elements (BSE) was designed originally (some 20 years ago) by Prof. Bernd Markert (Markert 1994a) to connect pieces of (analytical) knowledge concerning a set of different plant species most of which live near to each other in and around some bog in Lower Saxony (Markert, 1996) to features of biochemistry and bioinorganic chemistry. The principal approach was to compare abundances of elements (both metals and non-metals, >40 in total) among a larger number of plant species, producing pair-wise abundance correlations over the entire set of plants (Figure 1.13), by plotting for example, the analytically detected amounts of Al versus the corresponding Ca concentrations in the same set of (13) plant species (and all the other pairs).

Thus to produce an empirical relationship between abundances:

$[M]_{\text{species}}$ and $[M']_{\text{species}}$ of the kind:

$$[M]_{\text{species}} = k*[M']_{\text{species}} + c$$

Sometimes k can be very small, for example, when comparing abundances of rare metals like V to those of very abundant (but not necessarily essential) ones such as Al, and usually there is considerable scatter in the data (i.e., $r^2 \leq 0.15$), for example, for comparisons among (most) rare earth elements (Ce vs Pr, etc.), except Y. In extreme cases the above equation becomes almost meaningless ($r^2 \approx 0$, the

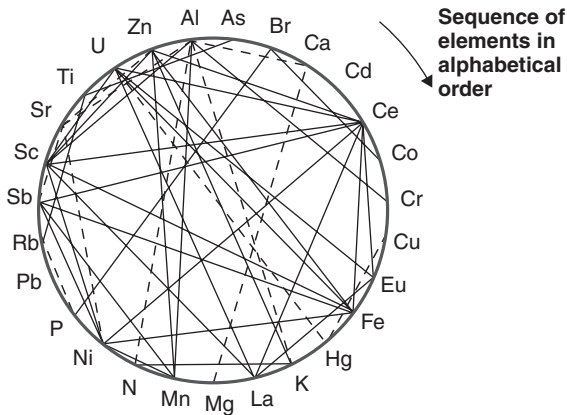


Figure 1.13 Element pairs that are either highly positively correlated (solid line) or highly negatively correlated (broken line). From Markert (1988).

concentration–value pairs being randomly scattered rather than forming some line, that is, across the set of plant species, the abundances $[M]_{\text{species}}$ and $[M']_{\text{species}}$ are not at all related), and in fact originally (Markert, 1994a, 1996) the focus rested with the correlation coefficients rather than the above original equations. These coefficients are given in the subsequent figure (Figure 1.14) which, notably, is just a cross-section through the entire space of correlations (>1000 in total number).

As a rule, Ca, Mg, Fe and Zn are the most abundant metals in plants, plus substantial though “useless” Al, lots of Cu in arthropods and mollusks both of which use Cu complexes (haemocyanine) for oxygen transport in respiration, and much Mn in green plants. In animals, compositions of major metals are similar, when considering soft tissues only, thus omitting the large amounts of Ca and the like in bones from analytical consideration.

But what is the chemical meaning of all this, and how is it related to chemical properties of elements which determine: (i) their chances/rates of uptake by roots/animals guts (from all food, water, sediment) and (ii) of retention, with usually a substantial extent of organotropy? When looking upon the majority of non-radioactive elements (+ Th, U), pairs of elements as defined above will combine all pairs of essential elements (say, an abundance correlation Mg/Zn, some 100 correlation pairs in total assuming some 15 essential elements, including the principal non-metals, except O), of one essential and one non-essential element (Al/Fe; Ba/Ca; some 200 pairs in total). Of course, also pairs of non-essential elements (like different rare earth elements; the large majority of entries) and, eventually, pairs which contain elements which are essential only for some of the investigated plant species (e.g., Si vs anything). The problem of abundance correlations may likewise be related to uptake pathways which sometimes are identical for two elements (Mo/B; S and As or Cr in strongly oxidizing, aerated conditions). Anyway, there is nothing like “biological groups of elements” akin to the periods of the chemical PSE: chemically similar or closely related elements may (different

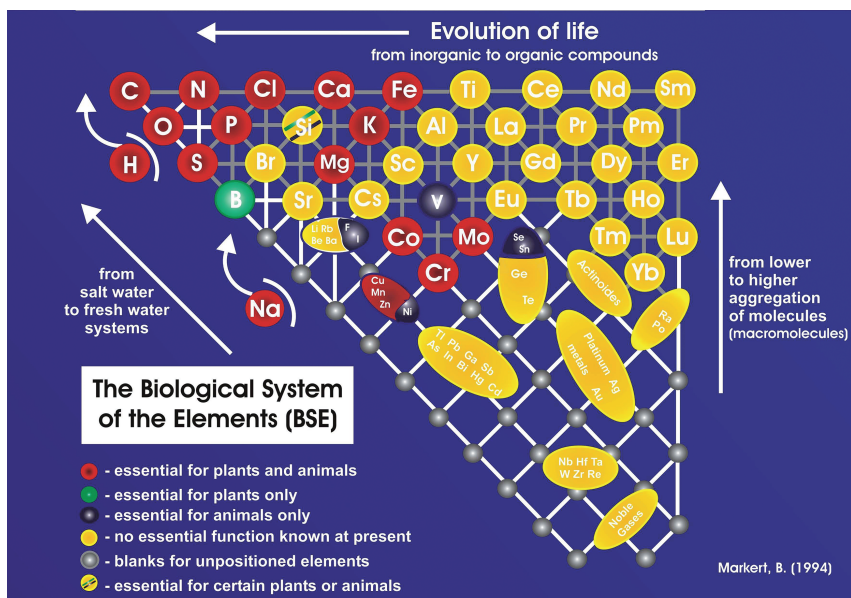


Figure 1.14 The Biological System of the Elements (BSE) compiled from data on correlation analysis, physiological function of the individual elements in the living organisms, evolutive development out of the inorganic environment and with respect to their uptake form by the plant organism as a neutral molecule or charged ion. The

elements H and Na exercise various functions in the biological system so that they are not conclusively fixed. The ringed elements can at present only be summarized as groups of elements with a similar physiological function since there is a lack of correlation data or else these data are too imprecise (Markert, 1994a).

rare earth elements, \neq Eu) or may not (P/As; Ca/Ba) get fractionated pairwise from the background in different kinds (species) of plants. Three features are quite important:

- 1) Chemical coupling in one principal (large turnover) metabolic pathway involving biocatalysts which do contain (and use) different elements;
- 2) Ecological stoichiometry;
- 3) Responses to some change in metabolic conditions.

Moreover, it must be asked to what extent are the responses due to external element composition, that is, fractionation, related to environmental conditions, or are fixed by genetics? The phenomenon of ecological stoichiometry suggests the latter to prevail, as do more deep analyses of biomass–metal ion interactions,⁸⁶⁾

86) The more thorough formal analysis by Fränzle (2010) proved for certain examples (e.g., birch trees; data taken by Markert, 1996) that the propensity of biomass samples (here, certain plant organs like

leaves) to retain some metals, comparing it to selective binding features of small-molecule ligands, remains untouched by whether these plants were grown on “good soil” or in highly polluted environs or even

while biomonitoring would not be feasible if this kind of biochemical control of chemical compositions would operate perfectly in variable environments. One reason for the latter is that there is no general way of removing excess inputs of elements, that is, excretion is less well defined with respect to uptake. Now, for the above three features:

- 1) *Chemical coupling*: oxygenic photosynthesis requires a balance between photoinduced activities of Mg- (chlorophyll, CO₂ binding protein rubisco) and of Mn-containing (photosystem II) biomolecules. Structures of all three molecules being almost universal,⁸⁷⁾ efficient water splitting and electron transfer (from water oxygen) to sequestered CO₂ will take some constant stoichiometric relationship of both photosystems: one (Mg-based) subsystem must reduce CO₂-bound to ribulose-bisphosphate originally—at the same rate (x molecules per leaf cell and second) as the other (Mn-based PS II) oxidizes water, save for some stoichiometric factor (which indeed is very close to one). Otherwise some substantial part of the electrons thus moved “uphill” will be “wasted” into either making elemental hydrogen (which nevertheless may happen in isolated chloroplasts) or CO₂ is absorbed and chemically bound without soon being reduced, making intermediates pile up with severe expenditures (“wasting”) of ATP. Because of the large dimension of this turnover in any photosynthetic organism, the larger share of both Mg and Mn are employed in this activity. One can predict the above Mg/Mn ratio in photosynthetic organs of green plants—regardless of its being leaves or needles—to be rather constant.
- 2) *Ecological stoichiometry*: in a more general reasoning, living organisms are found to exhibit some chemical composition which—within one species and concerning the most abundant biorelevant non-metals C, N, and P only for now—is about as constant as it would be in a daltonide⁸⁸⁾ molecule. Say, C:N:P = 3:1:1 in serine phosphate and $x:y:z$ in some (part of an) organism

on pure sewage sludge. Hence the chemical composition which provides the binding sites for metal ions (11 different kinds of possible ligands in the side-chains of the 22 proteinogenic amino acids alone) and controls the tendency for retention and sometimes accumulation of metals is actually given by genetics, with considerable differences observed in closely related (e.g., different *Vaccinium*) species (data taken by Markert, 1996).

- 87) Rubisco (almost entirely identical protein sequences) is likewise used by autotrophic bacteria and cyanobacteria to fix CO₂, and photosystem II also is genetically highly conserved even though the structure of high oxidation state mono- or

oligomanganese dioxo systems is not at all critical for their giving away O₂ by simple cleavage (“reductive elimination”).

- 88) The term “daltonide” refers to the early nineteenth-century British chemist Dalton who was stricken in some arguments with colleagues like Berthelot on the constancy of compositions of chemical compounds, maintaining this position. Now also compounds are known, however, which somewhat vary in composition (e.g., Fe, Mn, Nb oxides) without changing crystal lattice structure or decomposing into a mixture of discrete phases (“berthollide compounds”). The term “daltonide” thus now is applied to denote a constant chemical composition of a compound or, here, of an entire organism.

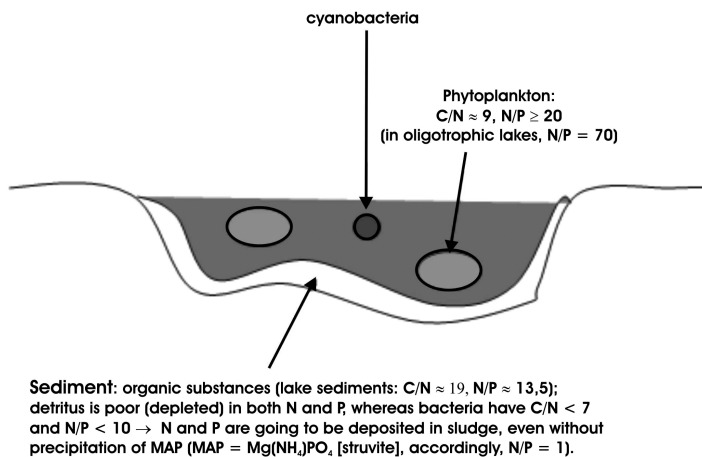


Figure 1.15 The variations among compositions of living beings in aquatic environments bring about either: (i) effective deposition of reactive nitrogen and phosphorus species in sediment or (ii) if precipitation fails, for example, for low Mg²⁺ levels, eutrophication

will occur even in the short run if atmospheric N is passed into the limnetic system by cyanobacteria (which contain and use nitrogenase) or by nodule bacteria in the rhizosphere of shore plants which are periodically inundated.

(here $x:y:z$ is to symbolize an undefined but rather general—and generally constant within a species or at least population—value of the stoichiometric ratios detected in biomass). Whenever living creatures are used in biotechnology to induce some matter transformations, these stoichiometric constraints will control the gross outcome; for example, it can be shown straightforwardly that in a sewage treatment plant the corresponding ecological stoichiometries of the involved microorganisms (include sulfate reducers in the CH₄-forming unit) preclude any complete removal of non-N₂ (odd) nitrogen from the system, with some nitrate or NH₄⁺ eventually turning up in open waters to which the cleaned sewage water is going to be discharged. Much the same holds for natural rather than constructed wetlands (Figure 1.15).

- a) Concerning the relationship between ecological stoichiometry and conditions of metabolism, it should be noted that the ratio C/N increases the more the weaker oxidants are at hand (Fränzle, 2010). Aerobic heterotrophs (animals, fungi) have C/N ≈ 7–10, while in sulfate reducers C/N > 100. In clostridia—doing some pretty strange H transfer organic redox chemistry at the very end of the chances to get metabolic energy from “ordinary” organic compounds—it may even be 200 (in wood, rather than the entire plant, yet higher values are seen which cannot hold for an entire organism as its principal chemical building-blocks all contain nitrogen).

- 3) *Concerning metals*, which make up but some small share of an organism for most cases, the stoichiometric ratios are way less rigidly regulated and conserved than for C/N, C/P, or C/S. Given, however, that most of the actual content of essential metals is really needed to effect some biocatalytic transformations, and different metals are employed in different metabolic pathways (e.g., Mo in many oxidoreductases, Cu in hydroxylations of arenes, Zn in glycolysis), abundances of such metals should respond to metabolic changes much more than those of C, N, P do. When ambient oxidants like O₂, NO₃⁻ or SO₄²⁻ are removed, there is no longer a need to store and apply molybdenum, while requirements of zinc increase. Experiments revealed that common baker's yeast *Saccharomyces cerevisiae* does behave according to these expectations when forced into alcoholic fermentation, but it takes many cell generations to actually adapt in this manner.

1.5.1

Specificity

The specificity of elements in biology has several dimensions. First:

- Some chemical elements are best suited to effect certain transformations, then:
- Biochemical features will enhance uptake rates of certain elements in some organisms (hyperaccumulation, most often of nickel), moreover:
- This is related to essentiality insofar as—as a rule, rather than *by definition*—essential elements cannot be replaced maintaining the corresponding biochemical or information-processing (e.g., in nerves) function in a given species (exception see below), and finally:
- There may be elements essential only to certain closely related groups of organisms (I in vertebrates, Ba in desmid algae, W in clostridia, and some archaea), yet another dimension of specificity linking bio(inorganic) chemistry and taxonomy to each other.

Hence, unexpected uptake of some element might give a hint of its having some function, however, certain doubtlessly (for some living beings at least) essential ones are employed in just tiny amounts (V, and Co in man: just a few µg/day). As far as is known now, there is *no* chemical specificity meaning that some chemical element would just induce or take part in a single (thus, specific) metabolic transformation, rather, some are used again and again in functions which apparently could be accomplished more conveniently using something else (Fränzle, 2010). However, the inverse kind of biochemical specificity is there: one given transformation (most of which are related to transformations at organic carbonyl groups, plus hydrogenations) is promoted all over biology by the same element or functional group (if any): Likewise, peculiar enrichments of certain (i.e., non-essential) elements often are restricted to one or few species only.

1.5.2

Essentiality

Essentiality is defined as and proven by experiments which show a certain element or co-factor (“vitamin”) cannot be replaced or omitted in diet of some organism without compromising at least its ability to reproduce; as a rule, it rather will die upon prolonged depletion. The list of essential elements is illustrated in Table 1.5.

If all the elements are present yet differing with respect to the optimal intake, the scarcest one will control and limit growth and vitality of the organism regard-

Table 1.5 List of (almost) generally essential elements (there are some exceptions even for elements like Fe, while K often can be completely and reversibly replaced by Rb; Scott and DeVoe, 1954) (top), with the additions and some substitutions which hold for certain kingdoms of life and sub-classes thereof (e.g., cyanobacteria).

Generally essential elements	
General	C, H, O, N, S, P, K, Mg, Ca, Mo, Mn, Fe, Cu, Zn
In higher plants	+ B, Ni
In algae	+ B, sometimes + Sr, Si, Cd, Br, I (discovery!)
In cyanobacteria	+ Co
In fungi	+ V, Na, Cl
In animals	+ Se, I, Na, V, Co, Ni, apparently As (V, Co, As in extremely small amounts), sometimes Cd; Na and K for information, osmotic purposes
In archaea	W replaces Mo; + Ni, Se
Elements involved in organoelement biochemistry	
Halogens F ^{a)} through I, As, Se, Te	
In metal bioalkylation: Tl, Ge, Sn, Sb, Bi, Cd, Hg, Co, Ni, Pt, Au	
Daily demand in humans $\leq 1 \mu\text{Mol}$: V, Mo, Co, As (“ultra-trace nutrients”)	

- a) Although fluorine was already detected in bones, teeth, ivory by the beginning of the nineteenth century, soon afterwards also spotted in blood, saliva, eggs, urine (Emsley, 2001), this is no proof that it is actually essential (cf. cerium in bones). In fact, it still remains doubtful that there are growth or reproduction difficulties in humans or animals to be linked to fluoride exclusion. Further, NaF is used as a potent insecticide against cockroaches and ants, and fluorocomplexes of whatever metals tend to be the most toxic inorganic speciation forms of these metals around. The number of biogenic organofluorine compounds is much smaller than that of each of the other three nonradioactive halogens, possibly due to quite another mechanism of fluorination required (except with benzenoid hydrocarbons: V-dependent haloperoxidases might also introduce fluoride or nitrite to afford fluoro- and nitroaromatics, respectively; O’Hagan, 2006). The case is equally poor with purported essentiality of chromium: in metal complex antidiabetic agents it apparently is the ligand 2-picolinate [pyridine-2-carboxylate, an isomer of nicotinic acid (3-picolinate)] which is active, probably after reacting with some metal in the body, as it does not matter for medical activity which metal complex of 2-picolinate [Cr, V, Zn, Fe(II)] is administered and otherwise Cr is just known to inhibit enzymes.

less whether there are excesses of other essential elements at hand (Liebig's law of minimum; Liebig 1840). In some cases, actually replacement is possible for entire organisms rather than just enzymes [Zn by Co or Cd in some marine phytoplanktons (*Thalassiosira* spp., Price and Morel, 1990); K by Rb in many bacteria and algae (Scott and DeVoe, 1954; see above)], or there are alternative metalloproteins in the "genetic store" of a species for the same purpose [phosphatases using either Mg, or Zn or Mn, nitrogenases which employ V rather than Mo besides Fe (Eady, 2003), or carboanhydrases which replace Zn by Cd (although of different protein sequence and molecule size; Strasdeit, 2001)]. Here, if complete substitution of elements usually as crucial as Zn or Mo might occur (and it does in some cases), a "soft" definition of essentiality is required: take one out of several elements which likewise could be useful for the purpose but then in sufficient amounts!

What is *useful* cannot be generally inferred from what a technical organic chemist would apply to effect the very chemical transformation (even disregarding metal catalysts which are too rare to be of general biological use, such as platinum group metals, or Re): there are quite many differences even when transport and modification of small molecules are concerned (Fränzle, 2010). In addition, it can be shown that selecting one element which is optimal to effect one specific reaction (or two) during evolution (e.g., ruthenium in a hydrogenase) will be not supported over generations in biology due to very deep-rooted physicochemical (limiting) conditions of reproduction (Fränzle, 2010). These preconditions, not to be discussed here, then are going to limit the number of essential elements, anyhow being just some part of the not so rare elements (completely disregarding ones which are as abundant as Al or Ti), but also using some fairly rare ones (like V, As, Cd, W).

Organometal chemistry, the gentle art of making and transferring organic groups or molecules at, to or from metal centers directly, though being rather versatile also in aqueous or lipid media, is hardly used in biology except for some CO and ethylene complexes involved in acetate synthesis, signaling, and for Co [vitamin B₁₂ (*cobalamine*), binding and transferring C-based anions directly fixed to CO in different oxidation states] and Ni [construction of formyl (-C(H)=O) ligands and reduction to methyl, CH₄ at Ni of Ni porphyrines in archaea]. The purposes of metals and Si in biology are:

- Biocatalysis (enzymes), mainly transport and activation of small molecules (O₂ at Fe or Cu; CO₂ at Mg; NO₃⁻ at Mo, phosphatases which use each of Mg, Zn, Mn or Fe);
- Information processing (nerve membrane; Na, K), control of energy- and data processing (Zn, Mg);
- Signal detection (Fe₃O₄, ethylene receptor in plants, Cu), but not for obtaining optical or acoustic signals;
- Supporting structures (Ca salts, SrSO₄, SiO₂).

Supporting structures—in animals and aquatic algae more so than in terrestrial plants—require far larger amounts of metals or Si, P than the other modes of use.

1.5.3

Bioavailability

Of course, an element or compound can exert neither essential functions nor toxic effects unless being absorbed by the organism (disregarding the capacity of ambient or overlying UV absorbers such as ozone, metal ions dissolved in water to shield against UV phototoxicity which requires the elements, ions or compounds be located somewhere in the path of sunrays rather than absorbed by the very organism). By dissolving in nerve membranes and in the synaptic gap liquid, even inert gases (noble gases heavier than Ne; N_2 , CF_4 , SF_6) may influence Na or K ion passages, diffusion of acetylcholine etc. and thus become neurotoxic (“nitrogen narcosis” and other kinds of “rapture of depth” observed in diving activities; Bennett and Rostain, 2003). So, before estimating the risk of an element becoming toxic to a target organism or even be transferred yet further to offspring (by all deposition in eggs, transfer via placenta, nursing in mammals, some fishes and amphibia), one must determine whether and to which extent it is resorbed at all in a specific mode, also influencing possible damages [it is more risky to the central nervous system (CNS) to inhale mercury vapor than to ingest Hg^{2+} salts, let alone compounds of monovalent mercury].

As a rule, only some—usually even small—part of the spatially accessible (food, water, soil in rhizosphere) chemical elements are actually taken up by any organism (typically, 0.5–20.0%); in fact, limnetic trophic chains are distinguished by thorough concentration maxima in phytoplankton and then stepwise yet steady decrease of element (in particular, metal—both essential and non-essential) levels in the series of consumers (Reichenbach-Klinke, 1974; Fränzle and Markert, 2002a,b). As this is due to losses of elements as complexes both via the kidneys and across the gill interface (Figure 1.16), then augmented by complex-forming acids in the water, trophic chains in water are short, with top-level consumers either breathing air (thus avoiding the effect of metal leaching by gills in top-level consumers, e.g., whales, including river-dwelling dolphins, seals, crocodiles, but likewise ospreys or bears) or large fishes consuming plankton, other plants (whale and giant sharks, grass carps, etc.).

Apart from this, bioavailability depends on:

- 1) Speciation forms in the environment;
- 2) Species which interfere with the elements;
- 3) Local chemical conditions which influence resorption.

In case (1), some rules can be given: fatty tissues or plant oils tend to accumulate elements which form lipophilic speciation forms. This will hold both for non-metals the compounds of which tend to be covalent and uncharged (except for acids, oxoacids) and for metals, semi-metals if undergoing biomethylation while metal ions are hardly lipophilic, except for a few (especially Li^+ , explaining its role in neurophysiology), also when forming rather covalent carboxylates (divalent Be, Zn, Pb).

Typical and most important in case (2) is biomineralization. Sr, the heavier alkaline earths and Cd, Pb, rare earth elements are readily taken up and deposited

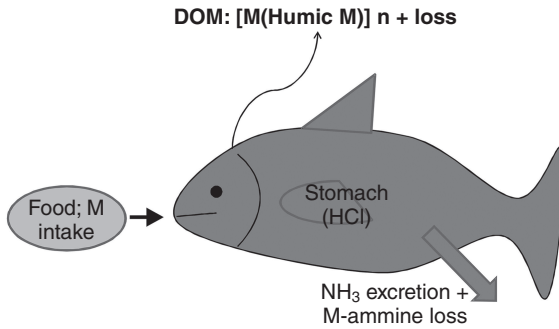


Figure 1.16 Intake and loss of elements around a fish. Ammine complexes will form and leach metals in the kidneys while organics dissolved in water (DOM = dissolved organic matter, including amino, fulvic and smaller humic acids, various nitrogen compounds) will cause extraction of metal ions from fish blood by complexation which occurs next to the gill membranes. When breathing water at a maximum dissolved O₂ content of some 10 mg/l (300 μM/l), a fish can oxidize at most 4 mg of organic (food)

carbon per liter of water passing the gills—and thereby releasing a few μg of the most abundant “biometals” to its own metabolism at most—will in turn pump all the external ligands dissolved or dispersed in one liter of water through indirect contact with its blood, so net loss along the gills is likely. In stomach, ingested, metals associated to protein- and other polymer-matrices are treated by dilute HCl, re-speciating some of them into chlorocomplexes (drawing by S. Fränzle).

alongside Ca in calcite or apatite biomineralizations, which among other effects enhances the uptake and subsequent in-body radiation doses of radionuclides like ⁹⁰Sr, ^{226,228}Ra. However, biomineralization depending on less abundant cations than Ca tends to be much more selective: SrSO₄ produced by certain marine algae contains appreciable amounts neither of Ca nor of Ba although the marine Sr/Ba ratio is not too large (about 500; Nozaki, 1997) and there are very considerable excess concentrations of Ca (Ca/Sr = 53 in Northern Pacific ocean water). Sometimes species from whatever kingdom of life accumulate elements without any reason to be seen: what will hickory trees do with rare earth elements (in particular, La) in their woody parts?

Generally speaking, bioaccumulation is a matter of both biochemistry (the chemical features which determine kind and strength of element–biomass interaction, starting with the peculiar chemistry of resorption in both autotrophs (from soil) and heterotrophs (from food and sometimes soil, water) and later being related to organ biochemical properties, and of the present speciation forms.

This is related to case (3): to start with the example which is both largest in dimension and most easy to comprehend, the alkalinity of ocean water (which is a buffer solution maintaining pH 8.3) causes most heavy metals to precipitate as hydroxides or carbonates. Hence dissolved levels of metals like Mn, Fe, or Cu are 1 nM/l or even less in seawater, and marine algae readily respond to Fe administration (ocean Fe²⁺ “fertilizing” experiments meant to enhance marine CO₂ uptake by photosynthesis). In freshwater, levels are four or five orders of magnitude larger.

Attachment of metal ions to soil polymers—humic acids and directly biogenic polymers from the organic soil fraction, including chitin, peptides—may block resorption as root-surface cells do not accomplish phagocytosis, as such large molecules or ions will not pass membranes by diffusion. Release is only feasible by metabolic decomposition—earthworms actually degrade humic matter and release compounds and elements attached to it, thus requiring peculiar protection ways to deal with heavy metals or As, Sb and so on. To avoid intoxication, namely, in-body precipitation of sometimes brightly colored sulfides (“do not eat yellow worms”). *Lumbricus* spp. earthworms containing As were found near a former As mine at Tavistock (Devon, UK); the latter is colored orange-yellow by in-body precipitation of As_2S_3 . Note that although As_2S_3 is very insoluble it is sensitive toward both O_2 and light (semiconductor photocorrosion), so the earthworm must cope with As, anyway as it will inevitably retrieve it upon humics digestion and it is re-mobilized in this aerobic organism if exposed to light. “Do not eat yellow worms” relates to the original title of a paper in *Nature* (Whitfield, 2003) where this first known case of sulfide precipitation inside metazoans—so far restricted to unicellular organisms like yeast—was described and discussed: bright yellow to orange refers to other As or Cd accumulation, while the even more toxic (Emsley, 2005) Sb will turn the worms dark red (and, with excesses of essential Zn an “innocently white” earthworm is obtained). For an earlier, more technical paper concerning adaptations of *L. rubellus* to just As and Cu, see Pearce *et al.*, (2002).

Besides degrading a matrix, bioavailability may also be increased by producing very efficient binding partners—such as hydroxamates, polyphenols or polylactons, cyclic peptides, particularly to sequester Fe^{3+} but also isocyanides in sponges (Simpson and Garson, 2004): when comparing which kinds of ligands are employed by bacteria, especially metallotrophic ones, yeast, and marine sponges to obtain or retain metals and transport after redox processes, one really wonders which are the primitive organisms given the simple compounds and procedures employed by both higher plants and also animals in gut resorption! Normally, in plants three or four different compounds are used to coordinate and resorb all the essential metals, save Na, K, Ca and Mo (about 7–10 left), that is, the ligands given away to the rhizosphere “must not” be specific in binding certain ions.

By the way, this non-selectivity, or versatility of metal ion ligation is also crucial for animals or fungi consuming plant materials: herbivory can only succeed, given the demand of animals and fungi for additional essential elements as compared to plants. Plants do not selectively absorb those elements which they need to run their own—autotrophic and thus more complicated—metabolism: a cow does “work” only due to plants using rather “primitive” ligands, and so does biomonitoring: Pb, Cd, As and the like could not be determined from analyses of plant or animal samples if they could not be co-resorbed “by mistake” (i.e., owing to poor cation–ligand binding selectivity). The above particular properties of bacteria, yeasts and other fungi in making highly efficient ligands have considerable drawbacks for rhizospheres in all since the latter also comprise such organisms in large amounts and biomass shares even if there is no specific mykorrhiza symbiosis:

ligands produced by the latter may mobilize metal ions in a manner that also allows for their (enhanced) absorption by plant roots around.

1.5.4

Toxicity

With every organism, there are elements, including some minimum set of metals (usually, K, Mg, Ca, Mn, Fe, Mo, Fe, Cu, Zn), required to maintain a number of biological functions, including:

- Catalysis;
- Information processing [not restricted to nerve membranes in animals but also covering, for example, the ethylene receptor controlling plant flowering and fruit growth/ripening, in which C_2H_4 gets bound to Cu(I)] and;
- Obtaining information (magnetite in bacteria, migrating birds, sea turtles and others).

In biocatalysis, often this function is related to attracting some substrate and/or a reaction partner of this by complexation and easing a chemical transformation by having it occur right within or next to the ligand coordination sphere. Of course, this kind of reaction critically depends on the “right” stabilities of complexes which combine all the substrates and the peptide/protein backbones which is also attached to the metal ion (and retains it within its polymer structure). Often, among chemically related elements like Be and Mg, Ca or most of rare earth elements/Tb the crucial difference between harmless or even essential and “highly toxic in general” just is that Be and Tb form too stable complexes (Figure 1.17).

Accordingly, an exchange of the central metal ion will, as a rule, disturb the balance among the involved compounds or ions or cause the products to remain attached to the center. Thus blocking catalysis (although there are some cases in which such exchange of metal ions in metalloproteins will even enhance catalytic activity, usually when Zn is replaced with Co^{2+}). Then, if another metal resides inside a catalytic protein, it is going to compromise biological function of this protein, producing a toxic effect on either the entire organism or some organs of it, thus, for example, causing infertility.

A telling example where a metabolic pathway which is quite common to different kingdoms of organisms is compromised by the same heavy metal ion in a specific manner (reaction mechanism), is synthesis of some porphyrine ring from aminolevulinic acid in all plants (Mg complex chlorophyll), animals, bacteria or fungi (Fe complex heme) which is commonly blocked by Pb^{2+} ions. Similarly Be^{2+} is highly toxic because it will replace Mg from crucial enzyme centers, and some carbamidinium salts and Tl^+ are (even more) so since transport of Na^+ ions by ion channels in nerve membranes is competed out, with these larger cations (tetrodotoxin, saxitoxin, Tl) sticking to the channels and blocking them.

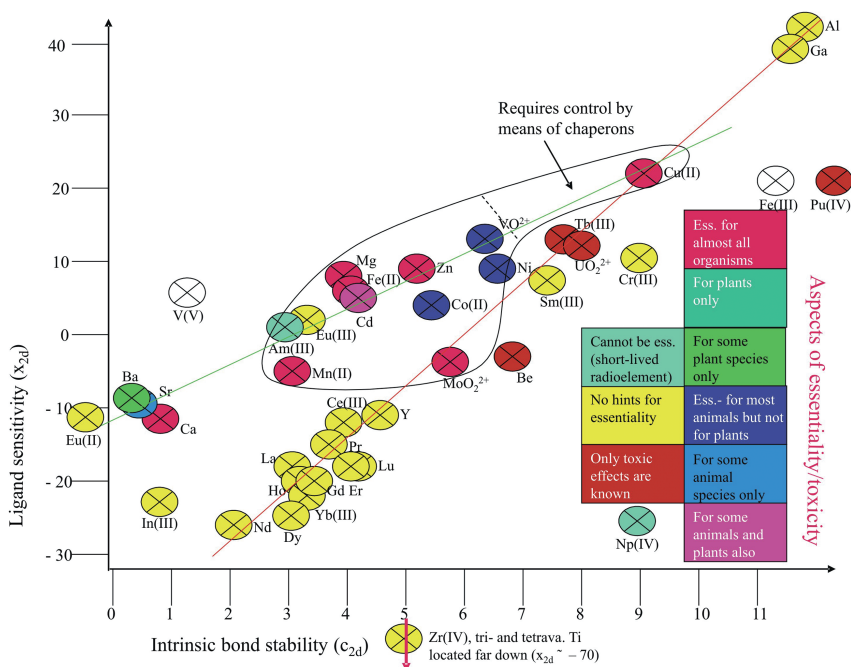


Figure 1.17 c_{2d} versus x_{2d} parameters of metal ions and essentiality. The exact values of c and x correspond to the crossing point of the lines inside the dot while the shadowing of this dot denotes existence and possibly range of essentiality (if there is any). While Fe(III) is absorbed by bacteria, it gets its biological functions mostly (exception: heme peroxidase) only after reduction to Fe(II); hence the symbol for Fe(III) is not colored at all. The actinoid elements U, Pu and Am are highly toxic but might be regarded either as radiopoisons or as chemical noxes. Both for uranium ($^{234,235,238}\text{U}$) and plutonium ($^{242,244}\text{Pu}$)

radioactive damages become negligible when compared to hazards by purely chemical modes of actions in the nuclides of longest half-lives (for those nuclides mentioned here: $10^5 \text{ years} \ll \tau_{1/2} < 4.5 \times 10^9 \text{ years}$) while there is no such isotope for americium ($Z = 95$; $T_{1/2} = 7400 \text{ years}$ for ^{243}Am , much less for all other isotopes); thus the different shadowing of the dots. The line which connects the essential divalent elements Sr, Ca through Zn, Cu follows a regression equation. Further information about this graph will be found in Fränze (2010).

By and large, the acute toxicity levels of essential elements do not vary in wide ranges, except for Mg, Ca which can be administered until getting close to causing osmotic disturbances [e.g., long-term ingestion of 5 g (!) Mg^{2+} /day apparently is quite safe]. Fe or Cu or Zn [with Cu^{2+} usually (not in every case!) causing violent vomiting upon excess oral uptake] are about as toxic as Cd or Pb (Emsley, 2005). An oral uptake of 200 mg uncomplexed divalent Fe will soon cause severe damage. Few elements are considerably more toxic (Be, Hg, Tl, As, Sb, actinoid metals—one can disregard radiotoxicity for long-lived isotopes) than the above, and Cd or Pb rather cause damages upon steady uptake over long periods of time; this is why

there are daily intake limits (e.g., 25 µg/day for Cd) more important in protecting people than the (relatively unspectacular) data on acute toxicity.

Metals usually differ from non-metals insofar as metal toxicity is less influenced by speciation, except for Cr or Sn, with dramatically increased toxicities often seen in organometal compounds if the latter are stable in water, including carbonyls. This actually is alluded to by the statement that “(heavy) metals cannot be degraded” – atoms of non-metals neither will “vanish” by chemical procedures but toxicities can be reduced more effectively in non-metals by changing their modes of chemical binding and/or oxidation states.

1.6 Information and Communication

Information, communication accompanied by re-considering the available body of knowledge and methods, contents of educating them is most important not only in pure and applied sciences but also in the realm of engineering. On regional, national and continental levels and across various periods of time, these are indispensable data required to understand and communicate especially environmental problems (Markert *et al.*, unpublished data).

In order to improve accuracy and sensitivity (lower thresholds of detection, detection of chemical species which hitherto escaped analytic procedures) of analytical techniques and measures of environmental technology issues of precision, reliability and reproducibility of certain methods gained ever more importance during the last decades (see Sections 1.4.1.3–1.4.1.4, 1.4.2.2). There are relationships and interdependences among information, communication and reflection on contents which were outlined recently (Markert and Fränzle, 2007; Markert, Fränzle and Tieben, 2009). Results of these considerations presumably bear fundamental implications for advancing emotional and rational, as well as technical (artificial) intelligence by education policies and bring about a novel process of education by dialog (Section 1.6.7).

In colloquial terms, communication is an exchange of information, describing a topic and activity which in itself contains (at least) two key issues:

- First, what is correct or wrong information, how can I produce or reveal it, respectively, proving the quality, that is, accuracy of information.
- Second, how and by what means can information be distributed and spread, giving everybody the chance to access and retrieve it regardless of its origins and contents.

One thus is posed to ask for issues of quality and principal meaning of information and its transfer for an advanced society, also regarding the risk of information being manipulated on its way. In the long(er) run, problems and paradoxes encountered there can best be tackled in the framework of “dialogical education” processes (DEP).

1.6.1

What Is This Thing Called Information?

Processing and transferring information now is crucial for achieving a sustainable, high-level way of living, besides addressing the problems related to use of matter and energy (see Lubchenco and Mehra, 2004; Huntington, 2000; Patrinos and Bamzai, 2005; Rosnay, 2000; Tiessen *et al.*, 2007; Walker, 2006). Information means to convert hitherto unknown into established knowledge (the Latin verb *informare* means to educate, to give things some shape). Recently these pieces of information is “encoded” by certain symbols or formulas, with humans made familiar with those codes in cultivated societies by explicit and lifelong learning, including professional education and personal engagement.

Figure 1.18 is to show how information is gained in a stepwise, open but never really completed multi-stage process (Roots, 1992). As a rule, measurements and other kinds of observation produce some set of data, thereafter selecting some of these data to obtain specific pieces of information and finally knowledge and recognition (Nefiodow, 1999). If the things thus understood can be judged about also in the later future, both the individual and society end up with a generally valid, secure plus of knowledge.

During the (so far) last steps of evolution, this way and process to gain knowledge at increasing pace was due to the vast (size and complexity) growth of the neocortex in anthropoid primate brains, with culture and learning by trans-

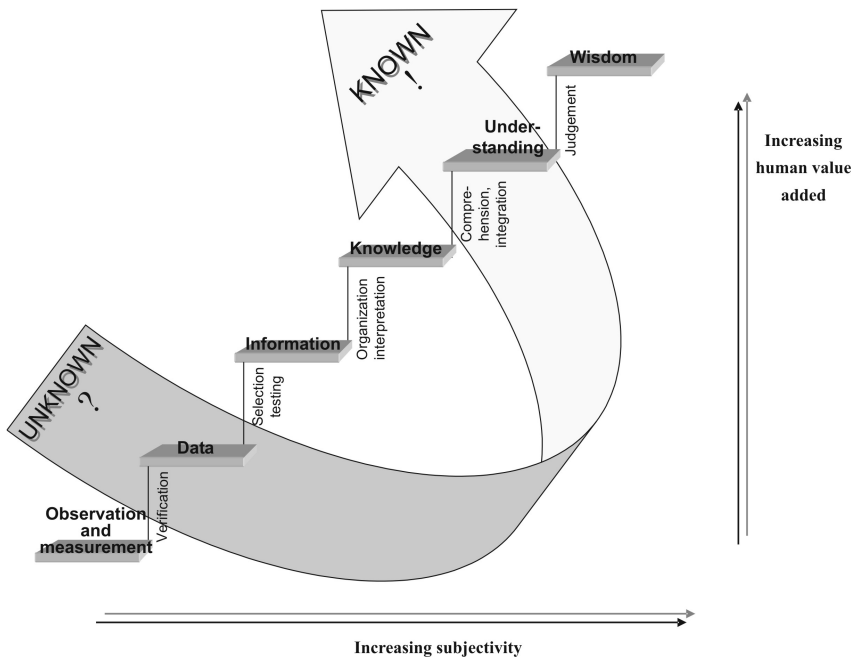


Figure 1.18 The staircase of “knowing”, modified after Roots (1992).

generational tradition (by parents, kindergarten, friends, school, etc.) giving mankind an immense gain of knowledge which is going on, now secured (by both acquisition and storage means like writing, electronic storage) and which provides the decisive competitive advantage among societies (Miegel, 2005; Biedenkopf, 2006; Kirchoff, 2006).

Within about 100 000 years,⁸⁹⁾ humans developed patterns of thinking and acting which permitted a most successful spreading across continents almost all over the Earth. Using education in a skillful and intelligent way—that is, selecting and applying solid pieces of knowledge—renders education the principal and crucial factor of future life (Hosang, Fränze and Markert, 2005; Markert, 2005).

For millenia now there has been another pathway of information besides scientific and rational investigation of our environs by (producing) information and knowledge, that is, religious beliefs (Figure 1.19). Lieth (2005) coined a term to distinguish between the levels of knowledge based on ratio and faith based on spirituality, namely telling apart real versus virtual information.

It has been shown several times that pieces of information belonging to (either) empirical knowledge or faith must be precisely and meticulously separated (at least here in the secular Western world), yet the gain of information and knowledge obtained by either path—empirism and faith—does not differ too much (Küng, 2005; Markert *et al.*, 2006; Ratzinger, 2006). Both faith and knowledge are rooted in pieces of observation, experience and hypotheses which are maintained only until they got clearly falsified (Popper, 1957). Hence one needs to ask and get criteria whether some piece of information is reliable (“correct”) or wrong, prompting us to consider the ways in which information is actually processed.

1.6.2

Information Processing and Communication—The Ratio and Relationship between Subjective and Objective Factors in Processes of Recognition

Hypotheses can never be “verified”, finally called “true”, not even in natural sciences, because during the development of man and mankind regularly completely

89) The notion that the spreading of modern humans all over the Earth (except Antarctica and southern parts of South America) took just a few thousand years is erroneous. Leaving aside the fact that *Homo erectus* did the same much earlier [being present in Spain, Georgia (Caucasus; Dmanisi excavation site) and Indonesia (Trinil on Java, next to Flores where the last *H. erectus* might have survived until a few centuries ago) >1 mio. years ago, later also in China (“Beijing man”) and Central Europe], the first few (tribes or individuals of) *H. sapiens* started to migrate off Eastern and Southern Africa some 200 000 years ago, to arrive in the

Middle East more than 100 000 years [Qefna cave, Israel (Mount Carmel)] ago, making it to Australia some 60 000 years ago and to northern America 13–15 millenia before now, about the time of onset of agriculture (“Neolithic revolution”) in both north western Asia (Anatolia) and the lower Mekong area (Vietnam, Cambodia). So the average speed of “migration” of *H. sapiens sapiens* to new territories was about 100 m/year, a group or tribe would thus as a rule not completely relocate “its” area required for hunting and gathering completely within a generation’s time, except when passing open ocean. See also Table 1.1 (Section 1.2).

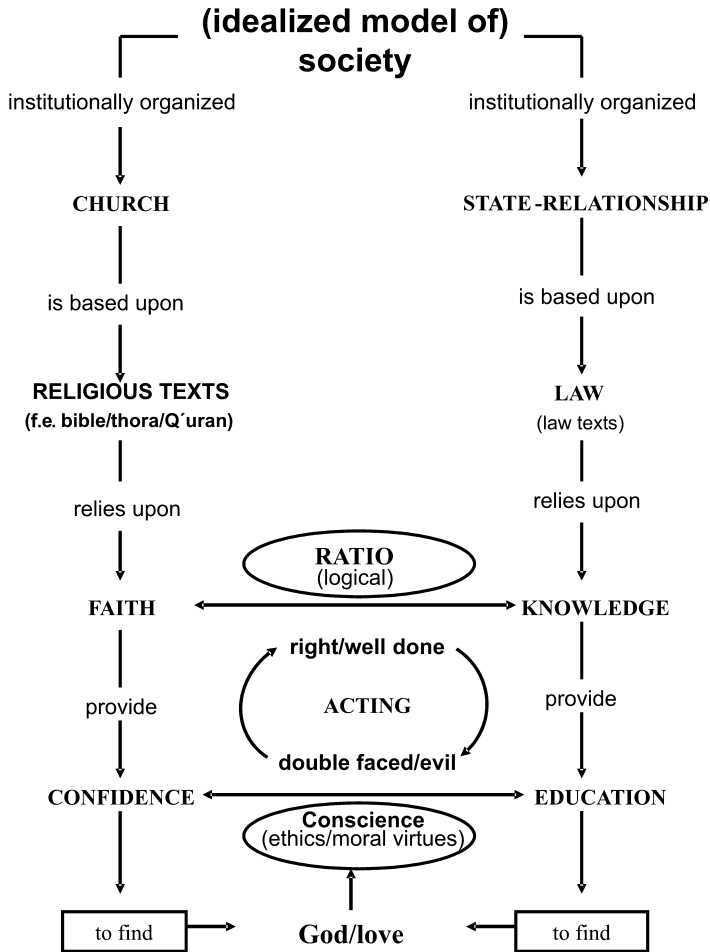


Figure 1.19 An idealizing model description of structures of society: the upper half is constructed by institutions including church(es), religion, state and law, while the lower-cultural-part is supported by faith, confidence, knowledge and education (taken from Markert, Fränzle, and Hosang, 2005). Convincement is brought about by linking

ratio (logical thinking) and conscience (ethics, moral) in a dialogical manner to separate right from wrong and good from evil. Self-confidence and education find their way into people loving each other, considered to be the only acceptable ends of society which may be negotiated. For additional explanation, see text.

novel developments and recognitions occur which were by no means anticipated and require steady renovation and re-consideration of things so far thought and supposed (Popper, 1957). In addition, there are fundamental problems from information (transfer) theory (Shannon and Weaver, 1976). Thus something now still considered “established knowledge” may tomorrow be falsified by experiment and hence dismissed as nonsense.

For example, in the nineteenth century physicists were quite convinced that atoms would not (inter-)change. About 1902 the reasons of certain anomalies in chemical reactions taking place involving highly radioactive samples became obvious, namely that, chemical elements in such conditions would not remain what they were (Becquerel, 1903) and correspondingly might behave differently next morning (Segre, 2002): they could spontaneously convert into each other, changing chemical behaviors⁹⁰⁾ also. Another rather dogmatic view—which, however, was challenged much earlier (mid-nineteenth century)—of similar kind was that biological species were constant, eternal—except for extinction—and not going to change anyhow. Now we know that organisms of all kingdoms are subject to constant development (or, rather, change) and that evolution is dynamic (Fränzle and Markert, 2006). A misinterpretation of some theoretical concept (Lewis's octet rule), combined with experimental difficulties, tempted chemists to believe the existence of (covalent) noble gas compounds to be impossible. Strangely, corresponding experiments in the xenon–fluorine system (Yost and Kaye, 1933) provided no isolable compounds, although both XeF_2 and XeF_4 (xenon di-, tetrafluoride–noble gas compounds) must have formed then and attempts made to intercept them with sufficient precautions (cold fingers) and so on.

In a sustainable information- and knowledge-based society, it is crucial to provide reliable answers concerning “right or wrong”, “subject to lie, manipulation or improvement”. In national economics, sound data on population development, unemployment rates and many more are indispensable.

Many citizens now doubt increasingly concerning an increasing number of topics, including wartime reports, environmental and economic data, whether there is any “truth” in those lots of pieces of pertinent information from most diverse sources, comparing it to their everyday experience, and finding it to be too “beautiful”, too optimistic or simply too positive (or else, negative). Nevertheless, published sets of data are the principal starting-point of any planning and making decisions for one's own future, and that of one's own children, arguments and methods must be found to estimate whether some purported “fact”, case or relationship is probably likely or rather unlikely; otherwise there is no foundation anymore to have matters settled by discussion and arguments. The way outlined here is mainly related to Markert, Fränzle, and Hosang (2005).

Objectivity and accuracy of information, so it has to be acknowledged, cannot be achieved on any arbitrary level of data aggregation, and hence data, opinions, predictions and their likelihood of being realistic depend on this very aggregation; it is pointless to demand objectivity if this aggregation level does not match, and in addition it must be considered when (or from which point onward) subjective

90) Conversely the concept of isotopy was developed about the same time (1911) when the nucleus of atoms was discovered: now there was a grouping of (itself radioactive or, rarely, stable) entities of very similar chemical behavior, now (from then on) considered all to be some kind of

lead or bismuth or radium and so on, regardless of what they had been or isolated from before. This approach eventually brought about the discovery of nuclear fission (Hahn and Strassmann, 1939).

feelings and opinions influence construction of an “objective” point of view once more. For explanation let us re-consider the stage model of Figure 1.18.

Observation and measurement produce data which then have to be subjected to statistical evaluation and selection eventually to become pieces of information. The validation of information thus obtained, combined with or done by interpretation and linking to already known facts, reorganization and coordination, turns information into knowledge. If density/amount and integration levels of new knowledge with “old ways of thinking” suffice, this process provides better understanding of matters hitherto investigated, with the knowledge to be stored for further use in libraries, electronic storage systems after multiple objective checks. So the steady increase of our knowledge should bring about some better understanding of phenomena.

As can be concluded from that stated before, understanding and proper use of information and knowledge imply some subjective judging of pertinent facts which—at least on a short term—is at odds with rational arguments and logical derivation. The ability of both individuals and social entities (groups) to learn, that is, to accept and process new observations, measurements, data, pieces and eventually knowledge continuously, is called “education” here (see Markert, Fränzle, and Hosang, 2005).

Accordingly we must accept that “pure objectivity” of data and statements is constantly decreasing up the “staircase of recognition” due to increased levels of aggregation. Objectivity diminishes with an increasing share and extent of single events/observations and linkages among them, producing relationships which are to be subjectively judged and viewed upon simply because “objective” measurement or reproduction are no longer feasible. What, then, is correct or wrong, true or false?

1.6.3

Ways of Producing Knowledge Established in Natural Sciences Lead Us Back to Accepting and Integrating Plurality of Views and Opinions

Recognition in natural sciences does regard subjective, even somehow speculative opinions and perceived facts as “true” (i.e., working hypotheses) as long as the opposite was not demonstrated. In fact, this process of collecting and formulating different opinions is called formulation of hypotheses; in this framework production of new hypotheses—including speculative ones—is accepted until they are falsified, exposing them as untrue.⁹¹⁾ Thinking in natural sciences thus disallows straightforward elimination of some—even apparently absurd—opinion before checking the underlying facts. And this is good, because it avoids an all too early elimination of unwanted approaches from discovering facts or alternatives for technical solutions in natural sciences like it might happen so often in (areas

91) Statements which cannot be falsified owing to their content or formal shape at all, are not considered true but rather non-scientific, let alone hypotheses. You

must distinguish this from axioms which likewise cannot be formally proven or disproven (falsified) but are useful in heuristic terms.

similarly exposed to) public opinion. In natural sciences, it is much more difficult to control opinions by forming lobbies than with a parliamentary debate. By providing a serious method of falsifying hypotheses, rather than premature dismissal of ideas and thus likewise protects “minorities” from being put aside and discredited too early.⁹²⁾

However, if this attitude of tolerance toward different opinions would be maintained generally, it would be hard to raise some democratic majority to tackle a practical problem or issue; accordingly asking for “right or wrong” at least at the base levels of data and information is required.

Telling what is “right or wrong” apparently is a task for law scientists, judges, attorneys, and members of the domestic secret service. However, also fundamental decisions in law are possibly flawed and thus doubtful for the very reasons given above, results from exact natural sciences shall be used to describe the way toward established knowledge. In analytical chemistry, concerned with methods to determine “what is present or absent”, the situation is very much like that what is to be done first in any serious analysis of society: doing a serious analysis of the present situation at first (Miegel, 2005).

In both analytical chemistry and all related branches of natural sciences there is a clear distinction between two terms, namely accuracy (rather corresponding to “truth” in law terms) and precision which just means that repetition of the experiment yields about the same measured data (in politics corresponding to social moods, opinions or trends; Figure 1.20).

Correct analytical results (statements of other kinds) cannot be produced by “democratic majorities” among a manifold of similar results (Griepink, 1990) but require rigid control protocols, like use of standard reference materials and mutually independent different ways of analytical measurement, making accuracy and “truth” of the obtained data most likely.⁹³⁾

The latter statements imply that terms must be used conforming to a common content before putting them into a wider context.

To give an example, take the terms “knowledge” and “belief” which used to be separated without much prior consideration into a pair of opposing views on the world, one which is based on objective experience and the other on some kind of transcendent religious statements. Doing modeling and applying systems theory

92) We are fully aware that this (critical positivism) is somewhat idealizing the way knowledge is gained in natural sciences. Max Planck once stated, bitterly, that there is no way to convince people in the path of revolutions in exact sciences but you have to wait for the proponents of the old position to get biologically extinct; this actually has a fundament in history of sciences, with Planck himself and Sommerfeld being the only prominent physicists born much before 1880 who eventually “accepted” and adopted

quantum mechanics, and H.A. Lorentz (1853–1928) “resorting” to electrodynamics and the basics of special relativity. It is just a historical exception when there are creative phases of just trying what can be done with a novel device or formalism (e.g., quantum mechanics during the 1920s).

93) This is not the place to discuss protocols of quality control in analytical chemistry in more detail; rather we point to corresponding textbooks.

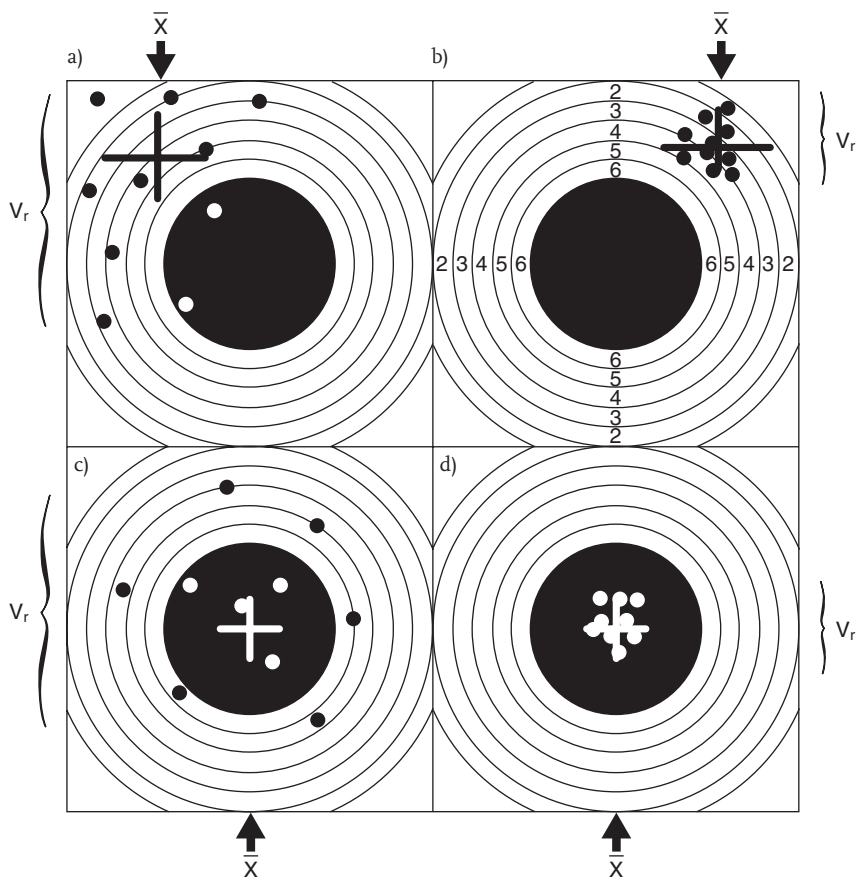


Figure 1.20 Illustration of the terms “precision” (reproducibility) and “accuracy” (the “true” value) in analytical chemistry (after Toelg 1976 from Markert, 1996): (a) Poor precision and poor accuracy, (b) good

precision and poor accuracy, (c) poor precision and good accuracy, (d) good precision and good accuracy, \bar{x} = arithmetic mean, ν_r = coefficient of variation.

to these terms shows, however, that either category relies on identical approaches, models and methods, producing common features and modes of behavior for in-group communication. Natural sciences rely on observation, experiment, but also prior experience and make use of knowledge produced and published earlier. Some biological phenomenon, for example, gets described, documented, possibly corroborated by some laboratory experiment⁹⁴⁾ and cast into some hypothesis. This hypothesis will be around until being falsified by another scientist. However, it often happens that scientist 2 obtains some other results which are not at odds with hypothesis 1 and thus can co-exist with it. Another scientist 3 adds yet more

94) Biochemistry, behavioral experiments, birds flying in a wind-tunnel and so on.

non-contradictory material to this and thus a pluralistic scientific community is created which cares about keeping opinions and meanings of terms objective. Of course this is no way of “moral quality control”, with this protocol both enabling, e.g., military abuse of scientific knowledge and tremendous achievements of human societies covering most diverse areas.

Now extend the above approach to faith: every religious statement, topic of faith can be verbalized, hence described, compared to others and possibly corroborated—or contested—by some experiment (see the manifold of scientific investigation on the Turin shroud). Even after this, the individual is left with “faith” as a kind of hypothesis that he (alone) has to maintain, by believing. People believing in something else do the same . . . One result was construction and stabilization of the five large world religions. These—like natural sciences—did achieve “incredible” things. However, wars “legitimated” by religious arguments or “God’s will” had and still have disastrous consequences.

1.6.4

Examples from Environmental Research

In biological systems, information does not just exist as genetic information only, but also includes chemical signals (compounds which carry information) which serve this purpose both within one organism (hormones, in animals also neurotransmitters) and among them, chemical signals which are produced by organisms and biocoenoses in metabolic activities which alters the respective environments, enriching it with certain substances while others are depleted. An exudate of the roots of a certain plant species can inhibit seedlings of another species from growth in the immediate vicinity. Conversely, this kind of information brought about by locally limited chemical effects and changes can also construct commensal relationships and even outright symbioses, causing one partner to settle where corresponding chemical signals do exist. Helmut Lieth once asked “how much information there is in a meadow”: answering this question includes to understand how organisms shape and structure their next vicinity, and (how) they do this by chemical means. Both horizontal and vertical, plant societies are rather diverse on decimeter scales, contributing much to the amount of chemical information,⁹⁵⁾ controlling the pathways and actors of succession by controlling which plants and animals can colonize some site only after corresponding changes of site and geobiochemistry (soil formation, changes in recently formed ponds, biochemical weathering and sediment formations) took place. The newly accessing organisms, of course bring about their own, literally specific, chemical and genetic information. Ecotones are key to such spatiotemporal processes because they

95) Chemical taxonomy of plants has it that related species share common products of secondary metabolism, including alkaloids, which can thus prove their being related. However, closely related species are unlikely to coexist at one site (competitive

exclusion principle), and mono-species areas are highly unstable. Hence, there is a trend toward high diversity of secondary metabolites in a rather stable plant community.

link different ecosystems and biocoenoses over steep chemical gradients (e.g., in a lake shore).

Moreover, there is a thermodynamic entity, namely entropy, which describes either the extent of disorder or the likelihood of spontaneous formation of some systems state. Entropy corresponds to information and reveals what are the limits of information passed along a certain channel over time (Shannon and Weaver, 1976): a state which can be produced by “shaking” some array of items, that is, by undirected modes of perturbation, is poorly ordered, distinguished by high entropy, however, low information (density). Biological systems are capable of introducing highly ordered states to both themselves and their immediate environment but only by exporting entropy and/or uptake of either electromagnetic (light, in photosynthesis) or chemical energy. Formation and spreading of biological information (reproduction, shaping of biocoenoses) inevitably includes destruction of other biological, biochemical or chemical information which, for example, happens during digestion. Metabolism thus brings about a spatial relocation of information, producing an inward (into the organism) flow of information. Accordingly such an active—which simply means: living—organism can be considered a transfer channel of information (to use Shannon’s term), much like a telephone cable, and the rules of information entropy handling apply.

Shannon’s classical treatment considers “white noise” as the outcome of information entropy production which eventually limits the transfer capacity of any single information transfer channel. In real environments, besides noise there is another limiting factor, namely the conditions required for growth and reproduction of present organisms. Here is a difference in effect between biodiversity and net metabolic productivity which both are used to describe a biosystem but are not directly related with or dependent on each other. Formally (high) biodiversity causes a(n increased) flow of information through an ecosystem which, to a first approximation, is proportional to the number of involved species⁹⁶⁾ while the number of individuals per species and generation period means informatory redundancy in Shannon’s terms (Shannon and Weaver, 1949), increasing information flow just by the logarithm of the number of individuals.

Accordingly, even small changes of biodiversity cause larger changes of information flux through an ecosystem than are effected by (even substantial) changes of its (net) productivity. Biotopes which are poor in nutrient- or energy supply (arctic areas) in both land and ocean are distinguished by a small number of species which however may occur in tremendous numbers, whereas tropical ones (regardless of severe nutrient limitations in coral reefs or Amazonian hylea) usually contain very many species, although net productivity likewise may be low. The latter kinds of ecosystems bring about a very large flux of information, with small redundancy (small number of individuals per species) causing larger decreases of information flow if one species is extinguished locally. The upper

96) “Species” here denotes a group of organisms which are a potential reproductive community. As reproduction is the key pathway for this information under consideration, the above species definition—which in biology is rather restricted to animals—does apply.

limit of information flow through one information transfer channel is given by Shannon's theorem.

Due to their very being signals, chemicals which are used in information transfer (e.g., hormones) also bear information beyond that encoded in their chemical structure. In metazoans there may be exogenous signals taken up from a polluted environment [as simple as NO (nitrogen monoxide) or highly complicated, like synthetic steroids or neuro-/psychoactive drugs], leaving the "informed" sub-entity (e.g., a cell or an entire organ) incapable of distinguishing whether these signals come from some other part of the same body or from outside.

As a result, there will be wrongful information processing, spelling deformations (action of teratogenic compounds, cancer), miscontrol of metabolism, loss of fertility and further deviations which may be lethal themselves or jeopardize some local population. Environmental chemicals, including phenols which bear the key structure motif of estrogens, halocarbons like 4,4'-dichlorodiphenyl trichloroethane (DDT) or PCBs and triorganotin compounds all are capable of causing sterility and genital malformations in mollusks, fishes, ice bears and reptiles. Although the annual consumption of steroids like 17-ethynylestradiol (EE₂) appears to be very small (some 50–60 kg/year in Germany), a simple calculation considering the annual total rainfall in Germany shows that even on average the biological action threshold for sensitive limnetic organisms (0.3 ng/l) is almost reached, in densely populated areas it will be considerably larger than this as sewage treatment plants will not remove it.

1.6.5

Performance of Brain and Modern Computers; a Comparison—Artificial Intelligence and the Internet

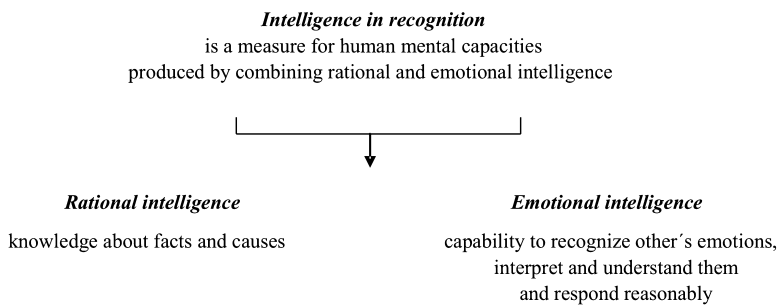
Regardless of the enormous progress in research on cerebral and neuronal functions of both morphological and physiological kinds which was achieved by medicine and natural sciences alike the tremendous complexity of the brain limits what is known about brain performance and its exact mode of control. Accordingly, the actual performance cannot be estimated either. While the human brain contributes just 2% to body mass, it takes more than 20% of oxygen demand. Because the brain is so active and too small to store substantial amounts of either oxygen or energy [glucose, nucleoside triphosphates (NTPs)] even rather short interruptions of blood supply can cause severe and irreversible damages of the brain. The total length of all the nerve fibers and axons inside the brain is estimated to be 5.8 mio. km, that is, 145 times the length of the Earth's equator (<http://www.de.wikipedia.org/wiki/Gehirn>).

Information processing occurs on a molecular level, starting with membrane-dependent potential differences which can be measured, up to (e.g., neuromuscular) the activity of the entire organism. While elucidation of molecular and biochemical mechanisms, down to their details, may be the everyday business of physiologically oriented neurologists, larger complexes of brain research, especially in description of specific cerebral processes, remain topics of present and

ongoing research. These topics include electrochemical interactions [what do electroencephalographs (EEGs) cause and tell?] and how far the brain consciously controls (by feedback) activity of entire of its centers, being in the center of recent research strategies and aims.

Often comparisons are made between the processing power of the human brain and that of the most modern computers. The brain is estimated to execute some 10^{13} to 10^{16} analogous process steps per second, as compared to 4.78 times 10^{14} floating point operations in IBM Computer Blue Gene/L (470 teraflops). The high performance of the brain is achieved by its many parallel operating connections among neurons rather than a high speed in doing single steps. While parallel architecture is common to the brain and high-speed computers, a biological (neural) network acts simultaneously as storage- and processor logic devices, which are separated in computers. This allows to re-new the entire storage content of a neural network during every single step while computer must and can only do this actualization step by step, that is, slower.⁹⁷⁾ One specific domain of informatic sciences is called artificial intelligence (AI) which strives to copy, reproduce and automatize “intelligent” behavior. The branch of strong AI tries to simulate and replace humans by constructing a kind of intelligence which thinks and solves problems like man does, being endowed with consciousness, self-consciousness and even emotions.

In spite of lots of corresponding attempts there is apparently no research strategy which promises to be successful into this direction. Rather, there is a recess to weak AI which means simulating intelligent behavior by making use of mathematics and informatics. Here, neither creating non-biological consciousness nor a deepened understanding of what makes intelligence are in the focus of interest. There are different forms of intelligence (not to mention the business of intelligence agencies . . .) which ought be defined as follows at least for the purposes of this volume and the forthcoming discussion (Figure 1.21).



Artificial intelligence is a technical product feature, e.g., computers and roboters may be endowed with by humans, which is accomplished both by peculiar kinds of software and by using sensors informing the system about its environment.

Figure 1.21 Simplified definitions of intelligence used in this volume.

97) (<http://de.wikipedia.org/wiki/Gehirn>).

Computers used for such purposes are called expert systems. Expert systems rely upon some data bank which stores specific pieces of knowledge. Hence the system is capable to tackle complex problems, cooperating with humans using it. Here it shall be investigated which are the conditions in which computers can mimic modes of behavior which would be considered intelligent behavior in living beings.

The internet, being an electronic network which connects smaller computer networks to provide fail-safe connections among “individual” computers for exchange of data. There are programs (algorithms) to retrieve specific data according to keywords or even verbalized questions. The recently best-known of these agents is Google, having a share of 83–90% in the German-language Internet. Google offers important pieces of information, representing all text files, pictures and videos, plus “free of charge” e-mail services and translations of foreign-language text files. However, Google also screens these e-mails for certain keywords and then abuse corresponding pieces of information for personalized advertizing. For example, when the term “car” repeatedly occurs in your personal mail traffic, you can expect to be hit by car advertisements in your mailbox.

Of course this raised criticism against Google for years (Bergere and Osmont, 2007), concerning not just the safety of personal data but also the issues of author’s rights.

In April, 2007, Google purchased the online advertisement firm DoubleClick, rising concerns among competitors because Google was already number one concerning text advertisement in search results, now possibly heading for a monopoly. DoubleClick⁹⁸⁾ now offered Google the pole position in online advertisement using pictures and videos also. Hence not just competitors in online businesses but also civil rights groups objected to this takeover at the United States Federal Trade Commission. Concerns on data privacy are caused by the protocols producing lots of data on individuals’ surfing behavior, data retrieved by both DoubleClick and Google. Personalized online advertisement just may be a nuisance but these data can as well be sold further or otherwise misused.⁹⁹⁾ Microsoft tries to compete by hostile takeover of Yahoo, investing some US \$45 bio.¹⁰⁰⁾

1.6.6

Emotional Intelligence

Intelligence as discussed refers to cognitive abilities akin to the neocortex which mainly supports logical thinking and acting.

Already in the late 1960s Joseph Weizenbaum, then with the Massachusetts Institute of Technology (MIT; Boston, Mass., USA), wrote the “Eliza” program to simulate the way psychiatrists talk to their patients, permitting the illusion of communicating to a real, human, soul-bearing speech buddy. Weizenbaum himself was shocked to learn the actual effects of this fairly crude program on humans—both psychically healthy and labile—and soon turned from a pioneer of

98) (www.doubleclick.com)

99) (<http://www.heise.de/newsticker/meldung/88379>; <http://www.heise.de/newsticker/meldung/90306>).

100) (<http://www.spiegel.de/wirtschaft/0,1518,532565,00.html>).

artificial intelligence (AI) to a critic of computers and electronic media (Weizenbaum, 1978).

During the past few years scientific research became focussed to another brain structure and kind of intelligence, called “emotional intelligence” by Goleman (1997). The structures which process the corresponding information are sited very deep inside the skull.

The cognitive brain—associated to the carved surface of neocortex—supports cognition, speech and thinking, whereas the emotional brain controls our personal emotions. After the emotional and cognitive parts of brain acquire some information from outside next to simultaneously, they can either cooperate fruitfully or compete for control over thinking, feeling and behavior (Servan-Schreiber, 2006; Schmid, 2008). Whether cooperation or competition prevails in this interaction determines our feelings and our attitudes toward the world and other people. With competition and “rivalry” prevailing, we feel bad and uneasy.

If, however, the emotional and cognitive brain support each other—with the emotional one shaping our life while the cognitive causes us to advance in this very direction prudently—we notice inner harmony, giving the foundations for long-term well-being (Servan-Schreiber, 2006). Because the brain is rather flexible, with different parts involved in certain functions, hence we cannot visualize states of either cooperation or competition among different brain features by optical methods. Nevertheless in some cases both deep and particular harmony acquired by meditation or effects of psychical diseases including severe depression may show up in anomal increased or decreased activities revealed by such methods.

Besides increasing the psychological contribution to healing people these works strongly influence cognitive psychologists (Gigerenzer, 2007), including research on effects of modern media on humans (Kast, 2007). Making use of this novel “emotional medicine” gives a chance to treat modern psychological mass illnesses such as depression, fear of future or stress to some extent without resorting to either medication or years of psychotherapy (Servan-Schreiber, 2006), as the “emotional brain” is in charge of many body functions and the corresponding parameters such as rhythm of heartbeat, blood pressure, hormone levels, functions of digestion and immune systems.

A very peculiar work deals with so-called savants, that is, people who, although often cognitively impaired, yet achieve extraordinary performances in some very small specific areas. Some 50% of the (rather few) savants are autists. The movie “Rainman” by Barry Morrow (script) was inspired by the actual life of one savant [although Kim Peek (1951–2009) was not an autist]. While savants apparently lack pronounced emotions, they can be capable of fantastic memory performances, including historical facts, or be remarkably creative in producing thoughts along uncharted ways (Einstein effect¹⁰¹).

101) Einstein himself probably was neither an autist nor a savant, being both highly emotional (although difficult in his most personal relationships) but fellow physicist P.A.M. (Paul Adrien Maurice)

Dirac (who theoretically conceived antimatter) and philosopher Ludwig Wittgenstein are now considered to have been suffering from rather severe forms of “autism-spectrum disorders”.

1.6.7

How to Shape Dialogic Education Processes (DEP) as a Future Principle of Communication

One needs to develop some generalizing concept to conceive a pathway into some information process which is all economically reasonable, ecologically responsible and maintaining peace between nations and societies. This concept requires to be theoretically sound and applicable to the economy, yielding the corresponding effective information and improving the present situation.

By now, correct information from economy, environment and social living conditions are not delivered to the majority of people in the World and, moreover, lack integrative reflection (Markert, Fränzle, and Hosang, 2005; Markert *et al.*, 2006; Tiessen *et al.*, 2007).

For example, Chinese citizens—some 20% of all mankind—are kept from uncensored access to Internet; additional billions of men cannot afford it. Is a “war for education” imminent?¹⁰²⁾

Needs and demands can no longer be met on the scale of entire (though still affluent) societies in either Germany or all of Europe. This once again calls for a concept which takes equal regard for the specific conditions and demands related to cultural history and the individual. Therefore, research on intelligence has to integrate cognitive and emotional processes of information.

Figure 1.22 depicts a scheme which combines multicultural common positions and parameters from natural sciences into a line along which “dialogical education” might arise and grow with time.

People of most diverse backgrounds need a common code of values and education which likewise regards individual demands and obligations toward society. Intelligence apparently includes a peculiar ability to produce relationships among different sources of information, with love and power being at odds ever since. While love (for yourself, for others, for nature) is in favor of positive relationships, power can be abused and thus promote negative relationships (Janisch, 2007).

The distribution and processing of information in this broad sense are and will remain crucial to analyze and understand whatever processes in environment, economy, and society. So-called “quasitruths” will vanish in the long term. Goudevert postulated years ago that “technical education without general education tends to produce knowledge without conscience”, introduced to us in Section 1.7 “Ethical aspects for society”, following Markert (2003).

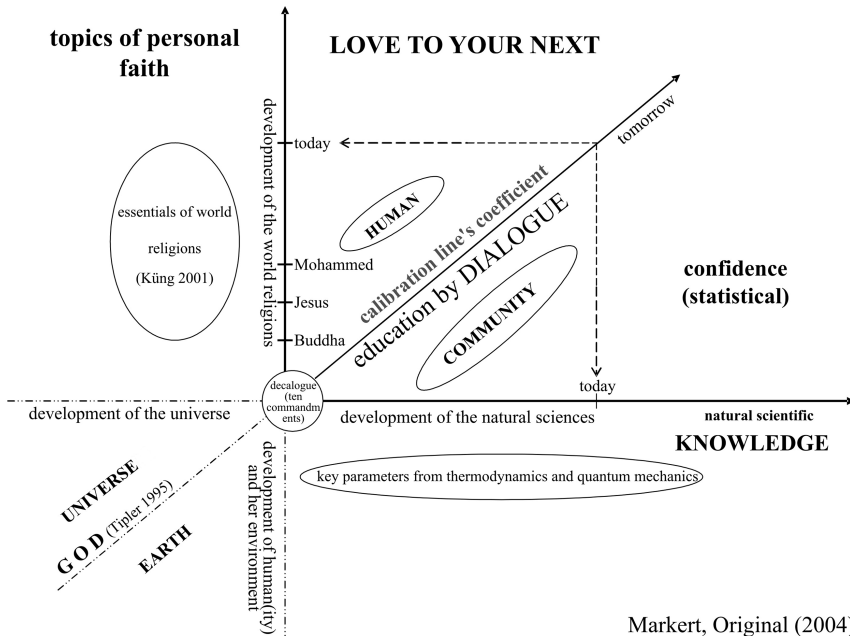
1.7

Ethical Aspects for Society¹⁰³⁾

While a globalizing society increases both its level of complexity and body of knowledge faster than exponentially (see Section 1.6), rapidly ongoing events and

102) (<http://www.laptop.org/-index.de.html>)

103) According to Markert (2003).



Markert, Original (2004)

Figure 1.22 Creation of information as “*de novo* synthesis” produced by linking knowledge from natural sciences, belief in world religions (from Markert, Fränzele, and Hosang, 2005) and by use of a dialog education process (DEP).

developments in all global politics and technology make crucial decisions necessary to be fastly done on short terms. In a parallel development, international economics, people who are responsible in politics or society or all those taking part actively in life of society, that is, citizens in the originally French sense of the word, must restart looking for values and standards which hold generally in order to maintain society living in peace and security for the foreseeable future.

In this section we embark from the historical development of market-based economies, a common notion on the essentials and principles of democracy, to get an idea of the present situation taking into account the increasing social awareness of citizens in a civic society. Technological advances on information, communication and biotechnologies must be supplemented by smart, high-value decisions on competence in society.

For these ends, education must be considered as an integrative task based on becoming aware of changes in technology, and those in international and global common convictions and politics to get international support. An intelligent dealing with conflicts, supported by a democratic-minded majority, for integrative solutions of problems is crucial, where mutual trust counts more than the text of some treaty, where diversity of faiths and opinions are considered a tool for obtaining stability while solidarity toward the weaker in society must become more than a mere idea or aim (ethical consensus).

1.7.1

A Market-Based Economy

Man ever aims at getting more and the best. In a surrounding which is noticed as a possible threat, the weak appear to be objects for domination, competitors are seen as enemies and wealth just is a reward for the achievements in producing something. This human attitude, seen from now to present and bygone results, appears to be purely egoistic from a subjective point of view. However, exactly these egoistic features of character and thinking enabled humans to out-compete most other species during evolution in the past 80000 years. Give and take, sell and buy, more generally speaking trading goods and services co-evolved along with cultural history of mankind, effectively cultural history could not be imagined to have occurred like it actually did without trade patterns.

Market-based economies generally depend on competition. At first glance, competition seems to cause hazards to individual existence since when one or two individuals (entrepreneurs) act on a common market and use it, this common use apparently mutually reduces their existence or at least performance (e.g., if their products are similar or they compete for the same group of customers). How well they perform and compete depends on their environment and living conditions, combined with specific bandwidths of tolerance and preferred conditions. Competition may change the notions of both tolerance (toward low wage levels, mediocre to poor living standards) and preference (high wage level, elevated living standards). Competition may occur on behalf of multiple primary and secondary mechanisms: factors among which the actors compete, such as customers, products, regions of marketing may be directly withdrawn, competition may be mutually inhibited by cartels or also dumping, or there may be modes of behavior pertinent to competition (threats, aggression, etc.).

Two quite similar entrepreneurs producing the same item for a limited system (market) will not coexist for long (independently). The reason is rather simple: it is most unlikely that the two entrepreneurs make exactly equally efficient use of some factor relevant in their competing, for example, of machines. Sooner or later one of them will perform better by their better use of the competition-pertinent factor. This entrepreneur is going to prevail, getting advantages from the ongoing competition. There is no reason to change or abolish this trend, and any system will just support a limited size of market simply for energetic reasons, hence the "worse" competitor is bound to vanish eventually.

However, almost every system contains entrepreneurs who are working on similar products and who (can) coexist. As a zeroth approximation the following rule holds: the more supreme (lacking behind) an enterprise is with respect to making use of its environment, the more (less, respectively) competition it may endure without getting removed by the competitors. Accordingly, the fewer similarities two enterprises display in their competition factors, the better and more easily the enterprises will coexist. Among very different economic niches, the chance will grow that competition to outside, toward other enterprises becomes less significant versus indoor competition.

To a nineteenth century entrepreneur, the worker/workforce was the most important factor in his enterprise. He was motivated by the longing to maximize private capital possession. This took people who would do the work in the enterprise; thus a historically novel part of society, the working class (blue collar workers) came into existence. The price (wage) to be paid for the work is given by “calculated work done per unit of time”. In all the ventures of the classical entrepreneur, value items are produced, which in turn create values in order to run a market economy. In markets, competition for customers is controlled and shaped just by supply and demand.

Later on, during the second half of twentieth century at least, it became obvious that exploiting nature by massively mining and using non-regenerative resources including hard to regenerate energy carriers [with this (ab-)use usually linked to an vigorously increasing environmental burden by pollutants which were released into the environment thereafter] was no longer accepted and tolerated by society. The phenomena observed then included the pollution of open waters, forest die-back, the Chernobyl reactor accident, the Antarctic ozone hole and possibly anthropogenic changes of global climate. Environmental problems thus arising and becoming evident were no longer an internal matter of the emitter countries because damage often arose also or even only beyond national borders. These transnational problems thus became international tasks also (Burtraw and Portney, 1991; Common and Perrings, 1992; Costanza *et al.*, 1997; Ellis, 1995, 2007; Fränzle *et al.*, 2005; Pearce and Turner, 1990). The Rio Convention of 1992 first had it that sustainability was to become the guideline to carefully deal with both nature and society on a global scales, with almost all countries being involved.

In several countries then legislation aiming to protect the environment was introduced and brought about serious criteria to be met by all branches of production and services (Elliot, 1995). However, generally speaking, these “green” developments of technology and legislation were only capable of tackling the so-called “external” pollution.

In this twenty-first century we are concerned with new kinds of problems which likewise call for novel ways of solving them (Beck, 1986; Biedenkopf, 1985, 1997); Markert, Fränzle, and Hosang, 2005; Miegel, 2005; Rosnay, 2000; Schellnhuber, 1998; Stern and Fineberg, 1996). Preconditions and tools to meet these tasks can be located “inside” humans, their psychosocial way of being, reflecting arguments and positions (which may, and often do, disagree) then to act in a manner which is distinguished by a high sense of responsibility for both oneself and others (Blackburn, 2001; Biser and Heinzmann, 2005; Choe, 2002; Ehrenfeld, 1993; Fromm, 1956; Hüther, 2003; Lapide, 1984; Norton, 1991; Rohrmann and Chen, 1999). Smart and non-violent management of conflicts—which is non-violent in both the material (no application of weapons) and the mental sense—will prove highly demanding both to the individuals and their views on public matters (De Young, 1993; Schwartz, 1994; Shrader-Frechette, 1988; Taylor, 1986).

Values like trust in some (economic) partner, a conscious promotion and protection of diversity, including different opinions in particular, and solidarity

toward those who “perform worse” in our society are values which will re-gain significance during this process (Farnworth *et al.*, 1981; Fischhoff *et al.*, 1982; Fisher, 1987; Gale and Cordray, 1994; Goulder and Kennedy, 1997; Hargrove, 1989; Meyer, 1997; Perrings *et al.*, 1995; Pickett, Ostfeld, and Shachak, 1997; Randall, 1988; Sachs, 2005). An intelligent handling of conflicts along principles given by trust, diversity and solidarity might prove key to developing an ethical consensus.

It becomes obvious that consensus apart from treaties depends and draws upon these values, rather than producing a contract or negotiating a compromise on some issue. In the future, the mere abilities of every single individual will shape motivation for living together in a society, rather than (over-)control by treaties, radical equality or social (over-)use (exploitation) of existing systems. These abilities refer to:

- 1) The ability to identify, define and honestly mention genuine conflicts and their reasons;
- 2) Act for a democratic yet speedy solution of problems based on free will and cooperation in a mind of partnership;
- 3) Do everything possible for man to realize solutions for corresponding problems jointly, sustainably and thoughtfully by all available means.

Modern results of psychology strongly suggest that individual “failure” in conflicts is an intrinsic problem in most cases and can be related to man having evolved from animals. “The strongest is going to prevail¹⁰⁴⁾” (by whatever means) is an idea that internally spoils individual thinking and habits of entire affluent societies, producing strong inclinations to make use of power, force and domination. How else can one understand that most individuals watch by media other people to starve (some 400 million children alone are below the level of “absolute poverty”, i.e., exposed to hunger!), and so do entire societies: this (non-)attitude can be considered a kind of terrorism (Gotzmann and Peschel, 2001; Henkel, 2002; Miegel, 2003; Sachs, 2005). This “inner pollution” of minds probably preceded and gave rise to the familiar “outer pollution”.

Among those challenges to twentyfirst-century humans, three must be mentioned which aggravate problems of global politics brought about and accompanied by fastly proceeding developments like those of informatics, communication technologies, molecular biology and genetic engineering. These challenges pose hazards for the further peaceful existence of the human race on this planet (Beauchamp and Childress, 1994; Markert, 2001; Osterwinter, 2002; Randall and Farmer, 1995; Schultz, Oskamp, and Mainieri, 1995). All three problems are capable of blowing up the web of society as we now know it; and more so if they interact they are really capable of destroying populations, which calls for an internationally negotiated settlement/agreement:

104) This is something quite different to Darwin’s principle of selective fitness “survival of the fittest” (in the given environmental situation and network of

demands and challenges) which obviously was both misused and deliberately distorted when transferred to principles of organization of human societies.

- 1) How to deal with the outcome of genetic engineering covering human reproduction also. Frankly speaking: what to do with those children born alive after “unsuccessful” genetic engineering and possibly considered a burden to society?
- 2) It is not yet settled how to get objective featuring of events in a multimedia-based word. Efficiency and mere speed of modern information and communication media can aggravate political miscalculations and wrong decisions if information is dealt with in an irresponsible manner (e.g., when reporting from war regions).
- 3) How to deal with convictions which are undemocratic, fundamentalist and often religiously underpinned? There are many examples from Israel, Ulster, the Basque areas, the United States and other parts of the world which suggest present democratic systems granting fundamental civic rights are (or were) incapable of meaningfully dealing with and opposing fundamentalists and other kinds of fanatics. The Kosovo intervention of 1999 was made by NATO—including German territory, airbases, pilots and equipment—without an UN mandate (thus avoiding a possible veto by Russia or China) in violation of international law!

History tells cruel lessons of what will happen if these problems combine and merge to bring about disastrous development, including genocide, propaganda, and fanaticism/fundamentalism.

1.7.2

Democracy and Its Limitations

Democracies deal with problems relevant to society by steadily balancing out the individual interests and common aims of society shaped by certain demands of acting in solidarity (Dahl, 1989; Dryzek, 1990; Pinzler, 2002; Rohrmann, 1994). Pursuit of individual interests must not restrain individual rights or even enhancing one’s own wealth, but likewise this clearly implies the duties of the individual to cooperate in a solidaristic community (Anscombe, 1958; Jonas, 1979; Kelly, 2006; Pearce, 1976; Rolston, 1994).

The state then is to provide and grant for some framework of laws and other rules that organize peaceful living together among citizens in a just, legal order. The state alone is allowed to use force (Figure 1.23). The rights and security of individuals are secured domestically by police and constitution-protecting services¹⁰⁵⁾ and many other institutions, while in international affairs the task of a state

105) Both authorities and judicial institutions in charge of protecting civic rights like the United States Supreme Court do. In the German original version of this text, *Verfassungsschutz* is mentioned (literally: Constitution Protection Agency) which refers to the German domestic secret service which is to observe and report on

(rather than curb!) extremist, antidemocratic or “counter-constitutional” political activities, be they left wing, right wing, islamist or run by sectarians such as Scientology. The *Verfassungsschutz* is entitled to take active measures only in terms of counter-terrorism.

Democratic forces and their functionality:

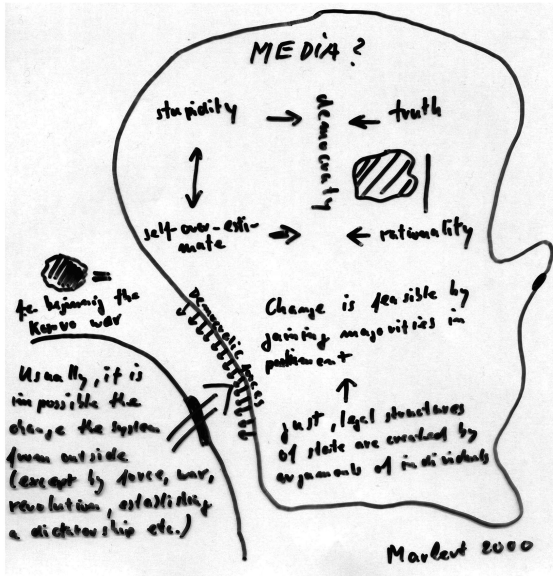


Figure 1.23 A simplified sketch of limits, boundaries set to a democratic system and its modes of functioning. The internal dynamics and stability of a democratic protocol of decisions release democratic forces and thus contribute to maintain rather stable limits of the system. Quality standards and smartness in parliamentary decisions grant for successfully dealing also with future, more complex and dynamic problem fields. The systems

requires stakeholders (politicians, entrepreneurs, parents, citizens) to steadily muse civil rights and duties of the individual and the solidaric society to adapt novel features to the system while avoiding biases, for example, in human rights terms and issues which would arise, for example, by deliberate violation of national or international law (Markert, 2003). More explanations are given in the text.

is to promote peaceful coexistence among forms of states which differ¹⁰⁶⁾ in both structures and aims. All states, societies and citizens then have their respective ranges of acting defined by the constitution. A system of law meant to balance individual interests and those of society gives a frame to oppose both individual offences (criminal acts) and extremist activities in society (e.g., those of left- or right-wing extremists).

106) However, in transnational structures like the Organization for Security and Cooperation in Europe (OSCE) or the Pan-American States Organization, some standards of democracy as well as peaceful procedures of settling domestic and international conflicts and achieving disarmament of the corresponding metaregions are

implemented even though not all OSCE member states actually conform to these principles. The European Council, for example, demands abolishment of death penalty by any state going to join and insists on the right to demonstrate for one's opinions, freedom of faith and the right to vote.

Further, the state support of peaceful coexistence within market-based economies must not limit individual freedom of shaping one's life too much, otherwise jeopardizing a "healthy" balance between individual and common interests. Free market economies simply rely upon individual initiative, his or her motivation and readiness to engage. If this readiness and corresponding individual responsibility is destroyed by excessive control of the individual activities by the state, markets (at least the legal ones) will break down. Such an excessive state control of individual activities and responsibility can also be caused by powerful administrative structures producing hierarchy and bureaucratic monsters which are capable of suppressing interests in private responsibility and economic activity.

Of course, specific kinds of religion can (and even must!) fulfill an important function in society, possibly producing even common senses of binds and duties in a society (De la Torre, 2004; Dürr *et al.*, 1997; Küng, 2001, 2005; Manzel, 2002; Markert *et al.*, 2006; Wabbel, 2004). Religions give incentives which provide an ethical orientation for an individual and entire (civic) societies. All over Europe, there are arguments from different notions of state and (vs roles of) society and of functions, roles of religious groups among "leftists" and "conservatives", "laicists" and those who promote a certain religion to play some role in society. These arguments are pertinent to the future role of Turkey in or beside an integrating Europe, likewise on the appropriate role and rights of orthodoxy: a "genuinely orthodox" shaping of relations between Church and state is an issue in all Greece and new European Union members Bulgaria, Romania, Latvia, Cyprus and so on. These differences in notions and concepts are borne out of different historical experiences also and become relevant if different ethnical groups meet, and they thus pose challenges to learning beyond borders. A kind of mutual trust in lieu of treaties will only be possible if this challenge is addressed. Notwithstanding this, a strict separation of church (religions) and state remains necessary.

Taking market-based economy and innovative power for granted and as the starting-point for improving understandings, concepts and structures of democracy, it still takes an arduous but probably successful way of optimizing systems soon for the generations to come. Here, methods of turbodemocratic¹⁰⁷⁾ implementation of urgent reforms and innovations are possibly useful.

1.7.3

Protocol for the Future: Grow along with Your Challenges

1.7.3.1 Thoughts on the Future

Often humans ask about the future: unemployment level predictions, stock exchange analysis, expectations on educational chances and outcomes, weather forecast for estimating whether one can have barbecue outside next weekend; these all require an educated guess of what is going to happen in the future.

107) "turbodemocratic" is a fast, high-quality process of decision-making during the identification and overcoming of problems, rather than the arduous, slow common approaches shaped by the wish of those involved to maintain their egos and powerbases.

However, “predictions are most difficult if they deal with future” (N. Bohr); this fact that the future cannot reliably be predicted, causing uncertainties and risks, is considered a dilemma because modern societies which cannot afford to improvise supply, which primitive ones would/could still do, require future development to be planned to some extent at least (Hill and Fowles, 1975; Markert, 2003). Hence, for example, population development (including demographic structure) and the spreading of diseases or epidemics must be predicted; and the use of non-regenerative energy carriers must be planned to obtain a responsible and sustainable society. On one hand, it is impossible to unambiguously predict future, on the other, we must do so to anticipate likely trends of development; this contradiction cannot be unraveled but we must practically accept it.

The principal reason why the future cannot be predicted is the high complexity of both functional and non-functional relationships in our environment, producing high dynamics, both endogenous and exogenous, in events and their changes. (Non-linear) changes in dynamics are best described by systems considerations using chaos theory, with deterministic chaos lurking in many features of developments most pertinent to our future. Of course, while the onset of chaos can be predicted, the state of a chaotic system after some period of unperturbed (or, worse, perturbed) development hardly can. Chaotic systems are most sensitive, amplifying the most minute changes in the starting conditions to large differences (Gotzmann and Peschel, 2001). To give an almost proverbial example, a butterfly putting a minimal turbulence to air when flying around at Hongkong might influence/“switch” the weather conditions in central Europe or northern America. Hence it is most difficult to obtain at least fairly reliable models which extrapolate spatiotemporal developments into the future covering the largest possible sets of starting parameters and their values.

Societies ever had to cope with future being uncertain; thus a glance into history might show which principal factors then shaped both technologies and society. The long waves of economy familiar under the term of Kondratieff cycles show that certain technological key advances are selected by global markets to “propel” the life of societies and global economies for quite a while (several decades). These crucial innovations include the steam engine, car and computer (Nefiodov, 1999). In highly developed countries,¹⁰⁸⁾ most citizens earned a significant improvement in their living conditions. Healthy food, high mobility, a large, diverse array of affordable items, but also communication and information and health sciences based on recent biotechnology are among the milestones that paved the way into some more qualitative and less sorrowful way of life.

Yet some two-thirds of mankind are still mainly excluded from this substantial improvement of life quality. Even worse, “affordable” workforce in so-called threshold countries [on the edge of thorough industrialization, like India, China (PR) and Brazil] is still used to maintain some difference in welfare, which is going

108) But it cannot be taken for granted that an already advanced economy will benefit from these periodical “pushes” to maintain a pole or at least comfortable position in global competition and development (cf. Argentina 1910–1950s).

to produce continuous decreases with respect to our common global political ends. The key area suffering from this is energy supply, with the remainder of affordable fossil energy resources going to be consumed during the next 50–100 years (in addition, releasing lots of CO₂). Furthermore there will be ongoing immense, and irreversible, losses of taxonomic species and of biodiversity, with annual destruction rates of primary rainforests being equivalent to the areas of about Switzerland or the Netherlands, without genuine substitution. Another urgent issue is to secure access to effective cures against epidemics like HIV/AIDS, which now are accessible for monetary reasons to only a small fraction of those most exposed, that is, in sub-Saharan Africa.¹⁰⁹⁾ People in “rich”, “healthy” economies could afford before, too.

With interconnections among different parts and structures of this world becoming ever more tense to end up in the globalization of technology, it is mandatory that all regions of this planet can take part in global markets as partners endowed with equal rights and chances. When there are political and economic instabilities in less privileged regions and states, this turmoil is going to destabilize the national economies of the wealthy North,¹¹⁰⁾ compromising our own standards of living.

Within industrialized countries, there are growing gaps between rich and poor also, with the chances/risks of social “rise” and “falldown” becoming more disproportionate than ever since industrialization. As a symptom of decreasing confidence in the future and its living perspectives, birth rates continue to fall, mis-shaping the demographic pyramid while trying individually to maintain an acceptable level of welfare.

Accordingly, gains in “organizing politics” which can be obtained from mere technological advances, with the aim of giving purely technological means to meet personal and inter-personal aims and longings, will serve by the way to maintain the present average level of life of an United States or Greek¹¹¹⁾ fellow-citizen, let alone further improve it.

Though translating economic interests into technological quality levels are indeed a lever to global economy, its actual positive political effects will touch only a small part of the world’s population. With the global population growing faster than exponentially (i.e., faster than ever before) while resources dwindle, counter-measures are most urgent.

1.7.3.2 International Quality Ends

While technological innovations are still needed, more success can be expected when trying to meet the life quality standards put forward by the World Health

109) Nowadays, there are programs in some of these countries, including South Africa, Botswana, and Uganda, to distribute antiretroviral agents, produced outside patent license coverage by exceptional agreements, for free to citizens who contracted HIV: one key reason for this is to avoid the breakdown of a qualified

local workforce rather than “mere” humanity.

110) Plus Australia, New Zealand.

111) This was written before onset of the 2008 financial crisis which hit Greece the hardest. But even before, living standards in Greece fell considerably short of most states in Central Europe.

Organization (WHO, 1996; Nefiodov, 1999). WHO states that almost all human beings, regardless of their places of living, cultural identities or other differences try to get:

- 1) Stable and positive self-estimate;
- 2) A positive attitude toward one's own body;
- 3) To be able for friendship and social relationships;
- 4) An intact environment;
- 5) A meaningful work done in healthy working conditions;
- 6) Knowledge about health issues and reliable access to medical support;
- 7) A livable present and a reasonable hope to have a livable future also.

Strangely, the roots of motivation of average German entrepreneurs to perform and live better in the framework of socially responsible market economy closely match the aims in living of every other man in the world, notwithstanding his/her occupation and site of living. Accordingly, we can hope that a means to improve conditions for everyone's quality of life should be found according to a common set of integrative approaches and measures, provided there is serious and honest interest in this.

1.7.3.3 Learn How to Learn

Hence it will no longer do in the future to use technocratic pieces of knowledge to obtain these integrative approaches to overcome the present problems, since:

- Increasing dynamics and complexities of problems need a better, more reflected arguing on pros and cons of some strategy;
- Crucial (or better: all future) decisions can (ought) be done exclusively based on provable, objectively stable pieces of information, data and knowledge, while:
- Sufficient transparency (in Russian: glasnost) must be provided to all the stake-holders.

With "performance being the personal ability of an individual to change and adapt", it takes "education providing the ability to be open and ready, able to learn on all levels".

Dealing with conflicts smartly and trying integrative problem solutions are more closely linked to each other than hitherto used to be assumed. Hence, life-long learning, achievement of quality and competences will get an ever larger relevance both to secure our common future in the society and for personal lives in the spheres of work and profession, family, leisure time, culture and politics likewise. The individual has to develop his ability to learn for this purpose and keep on learning as the way to obtain personal competence with regards to social, occupational and methodic acting (BMBF, 2001; German Federal Ministry of Education and Research). Concerning economy and society, these competences become crucial factors for innovation and capability of social self-structuring in order to compete successfully on an international level rather than losing contact to recent social and cultural developments.

We now need a broad movement to promote life-long learning both to develop and maintain individual living chances and to keep socially oriented democracy¹¹²⁾ fit for the future with regards to its economic, ecological, cultural and social perspectives of further development. The system of education must provide the basis to achieve this, given its ends, contents, structures and ways of acting and teaching (BMBF, 2001).

Life-long learning does not just mean to involve as many citizens as possible all over their life-phases (at least until retirement) but has qualitative drawbacks on education policy also. Life-long learning requires to change the attitude toward learning (BMBF, 2001), making learning a process the individual must pursue and shape all along lifetime responsible for him- or herself. With economic innovations and changes in society occurring ever faster, there is responsibility to autonomously adapt one's kinds of qualification. A new cultural sense is required which integrates learning into the processes of everyday life, acknowledging this and fairly estimates outcomes against the difficulties of this process (BMBF, 2001). Classical forms of learning and education offered by schools, professional training, university or secondary occupational education will not lose their significance but must be corroborated by a new key feature of informal learning, which takes place in the "school of life", in social networks, everyday life, at workbench, in family and leisure time. This is really a new principle of learning which must be developed, focused on one's own responsibility and capability to shape this process individually and autonomously (Dahrendorf, 1986, 2003; Goeudevert, 2000).

With a high degree of individual responsibility and autonomy being required, motivation and support of hitherto less advantaged groups must not be disregarded; these groups otherwise would not be capable of fulfilling such a task of self-motivation and structuring, as a rule. Education politics and practical education rather must be concerned and aware that nobody is taken off his educational and career chances. Groups who are now almost beyond the reach of education¹¹³⁾

112) In the German original: "*soziale Demokratie*". This term does refer/allude to "soziale Marktwirtschaft", the concept put forward by later Federal chancellor Ludwig Erhard (1897–1977), sometimes also dubbed "the Rhineland way of doing capitalism" rather than, for example, "Archiv der sozialen Demokratie" which is the central part of the party archives of the German Social Democratic Party (SPD). Anyway, in Germany the link between democracy/federal structuring of state and social norms is part of the constitution and even officially protected against any change (*Grundgesetz* articles 20, 79, 116).

113) In Germany this really became a popular term: "bildungsferne Schichten" (people

who live in utmost avoidance of education). The Programme for International Student Assessment (PISA) studies revealed Germany to be the one country in the developed world where educational and thereafter occupational chances depend most on the educational status (and income levels) of the parents, more so than even in many developing countries. So a vicious circle can be established (parental poverty precludes education of the children to a level now required even to obtain a reasonable apprenticeship position) which is avoided only by more active measures pointing to the corresponding milieu and urban neighborhoods.

must be integrated to avoid producing new obstacles in obtaining education and training. The present serious level and extent of exclusion of people and groups can be reduced in the near future only if the array of educational contents and kinds becomes more closely related to ongoing economic, cultural changes and those in society, while the offers must become more focused to the demands of any individual (BMBF, 2001).

With life-long learning becoming the paradigm of education, tasks and structures of classical agents of education must also adapt. A culture of learning which conforms to recent demands takes more and novel kinds of coaching and services, but also needs an enhanced degree of flexibility, self-responsibility and communication. These in turn require novel kinds of partnership with “consumers” and users of this broadened array of education. Institutions of education and culture, those concerned with social and youth welfare, clubs and enterprises, single persons and the activities of all of these must be pushed and motivated to investigate novel ways of learning by new kinds of cooperation (Hosang, Fränzele, and Markert, 2005; BMBF, 2001).

1.7.3.4 Transborder and International Regions of Education

Border transgressing regions of education which provide the chances of life-long learning working, and education to all childrens and youngsters but also parents, teachers and other adults, must be promoted better than before and get (placed) into the focus of public interest. Of course, diverging interests of political powers and parties, regional and national particular notions and interests will persist on either side of the border but there are also local commons which are a topic of (transcultural) education as such and itself can and must reshape present topic-focussed into ability-focussed curricula of education. A higher level of education becomes more attractive when people notice in remote border regions also: *tua res agitur*; it is your (local) matters that matter, rather than (just) the views and issues of some far away metropolitan region, far away in both topographical and mental terms. Besides better ways of overcoming local problems, this will enhance the wish and positive feelings on life-long learning, producing competences, self-confidence and thus finally increases occupational chances in border regions also. By the way, a kind of education defined and constructed like this is going to both catalyze and pay itself in the long term mainly.

There are plenty and more of historical burdens and present deviating interests; hence the first step must be constructing an integrative mode of conflict management on the very site which there gains support by some democratic majority. Rely on trust rather than treaty—this will work only if the above attitude is given. Diversities of opinions and religious faiths will only become a bonus and a chance to achieve more stability if we become aware of some ethical consensus which can be learnt and which is going to link us, including Muslim or agnostic fellow-citizens. This ethical consensus will include the tolerance of other positions and beliefs and likewise solidaristic acts toward the weaker.

1.7.3.5 Think Tanks Can Be Sites and Means of Smart Conflict Handling and Identify Integrative Solutions for Problems of Society

Problems and questions which recently arise in society are distinguished by multi-disciplinary and international ranges, hence highly specific expert knowledge and corresponding skills will not do to solve or even characterize and define such problems but it takes the readiness of everyone who is involved to mitigate among the often most diverse individual interests and wishes. Hence the crucial feature of an integrative problem solution rests not so much with technology or funding but with the actual “ability of everybody to honestly and convincingly achieve a solution which is acceptable to all the stake-holders”.

There are many features of conflicting double-binds in modern societies: politicians and the parties which “made” and support(?) them, officials including university professors in public service domains and authorities, physicians and their medical responsibility and ethos, TV producers and TV watching quotas, mothers and fathers who want both to perform and progress in occupation and responsibly, sincerely rise their children, they all are faced with conflicts which cannot be resolved and block potentials for overcoming these and yet other conflicts even though all are convinced that it takes genuine professional ethics, genuine convictions and their active realization in everyday life to ensure a sustainable and justly motivated structure of society!

In many different societies, psychological obstacles to adhere to these rules are posed by many citizens who already became solidly mistrusted and alienated by actions and premises put forward by politics itself. This alienation is but a symptom but it can block a real, honest dialog in society which is devoted to solving problems by innovative modes of thinking up to the point that it becomes impossible. Hence Miegel (2003, 2005) is quite correct in demanding citizens be fully and honestly informed about the situation before even starting a public discussion on how to deal with it, including the side-effects which would arise if the actual situation is neglected any longer. This will be the first rate of a “pound (weight) of honesty”: politicians and others in charge of decisions pertinent to society must be courageous enough to be (recklessly and fully) honest. Viable data on the situation and complete transparency toward all ones who are or could become involved are self-evident conditions to get any reasonable acting which can make a meaningful future.

1.7.3.6 How Much Time Is Left for Solutions Taking Care of and Integrating the Present Problems?

Realistic estimates of the time left to mankind to tackle problems in an integrative manner on global scales, implement and complete them range from 500 to 1000 years from now. Table 1.6 gives the necessary or possibly optional conditions and steps for this kind of global change. Maybe by 3000 there will be some merger between human and nature shaped like a symbiosis (Rosnay, 2000). This would be a harmonized balancing of all the inputs and outputs among all the existing biocoenoses for common and mutual benefit which to plan and realize must be the priority and aim of all human activities then. To achieve this end, it will take

Table 1.6 Global trends of development predicted for this new, just beginning millenium.

By 3000: Man joins a symbiotic relationship with society and the ecosystems in order to survive. He is going to become a symbiotic cell of a huge planetary organism starting to live based on itself: a macroorganism on which our future depends (Joel de Rosnay, director of the museum of future technologies at Paris; Rosnay, 2000).

By 2500: A just world can only be created if the last dictatorship has been abolished providing the key condition for global justice which is peace. This is going to happen 500 years from now (Goeudevert, 2000).

By 2100: Assuming a further exponential development/increase of our mental capacities for a conflict management which becomes most urgent in the future, the recognition that a more just future world cannot be achieved without global peace will set foot all around the world.

By 2030: Creation of the precondition (by 2022–2028) to abolish the present state of “hunger terrorism” which hits large parts of Africa and to put an end to it by the end of this century (“turbodemocracy;” Markert, Fränzle, and Hosang, 2005).

1000 years of global education, which must of course be developed, discussed and effectively implemented for gaining acceptance among all mankind. The practical result which is inevitable is to agree on a globally common criterion of completely just distribution of material and non-material goods and items among all people living on Earth. Before this can be reached, constant global peace must be achieved, which will be about 500 years in the future. In addition, this will be the period of time until the downfall of the last dictatorship on Earth. This is another precondition for the era of stable global peace predicted by a number of colleagues, which in turn is indispensable for justice in the above sense, namely the just and balanced distribution of all the essential goods.

Table 1.6 gives an idea of the timescale it might take to implement the necessary changes in a “turbodemocracy” once there is common acceptance of education being most urgent: until 2030. This is the period of time it will take to harmonize and equalize in rank intercultural and intracultural activities regarding the many diverse spheres of interest—national and international, mono- and multidisciplinary, regional and transregional. There is a desire to give, to share, to understand and to accept other people and cultures which is corroborated by enlightened self-interest, acknowledging that this is the only feasible way to possibly and satisfactorily ensure one’s own existence, and this promotion by enlightened self-interest will make us “donate” education and professional training to entire parts of continents such as Black Africa within one generation’s time, about 30 years from now. To realize and implement this will become a common task giving the chance to live in about the decent and self-determined way of decisions after all which we are completely accustomed to. The latter global process may be completed by 2100.

1.7.3.7 Conclusion

Questions and demands of future will not depend so much on the way to decide whether a new street is planned for purely economic reasons or canceled to protect the environment but how fast and efficiently a decision can be done which satisfies all the involved by some consensus. The “mental blockers” mentioned above are often going to block rational and reasonable solutions, removing the chances of gremia and councils to decide and act successful and efficiently; thus think tanks which are focused on jointly finding problem solutions are most urgent to establish (Pinzler, 2002). Think tanks are established in United States political counseling for as long as project teams last and they cooperate for several months. These teams are completely independent of political parties, industrial and other lobby groups and are distinguished by utmost competence on their issues; thus they can develop and offer stake-holders some recommendation how (on which way) to solve their specific problem.

Think tanks can be associated with schools, universities or other sites of (occupational) education where people meet, live, develop, negotiate and face arguments. Likewise think tanks can be private institutions (other than private universities) where specialists trained in interdisciplinary thinking create both fast and realistic solution approaches. This can shorten that almost infinitely long, bureaucratic and unbearable route from identifying the original problem to the supreme decision maker and serve to relocate the solution next to its topic. Creative potentials of those taking part are considerably enhanced, increasing readiness to find solutions by personal considerations, experiences and understanding. Think tanks are not primarily challenged with time shortages, while honestly telling that a problem cannot be solved by now because of lacking capacities and pieces of information would suffice to avoid decisions which are premature or outgrowths of political bias. Regional think tanks can thus be a valuable and important tool to develop new strategies, ideas and finally innovations.

This means education and professional education will decide about life chances in the foreseeable future (Figure 1.24).

Everybody needs education! Once this is generally acknowledged (hopefully soon), there also will be substantial funding for all respects of education. Parents, children, pupils, students, teachers, people in occupation and retired ones will see and be able to attend informal colleges,¹¹⁴⁾ kindergartens, integrating centers where youngsters, elderly and other people meet, elementary, occupational and highschoools where both teaching and learning are fun again, aiming to be a little better than your neighbor while sharing joy with learnt matters can also go without saying once again. “Knowledge must turn into love” (Choe, 2002). Smart management of conflicts and integrative ways of dealing with problems thus are very

114) In original German: *Volkshochschule*. These are public institutions which have their part in advanced (not apprentice) professional education, besides universities and universities of applied sciences. There are also courses in

computer skills or various modern languages. Some certification of courses at *Volkshochschule* can actually be used in a profession, unlike a university; an *Abitur* (school leaving examination) is not required to attend.

