

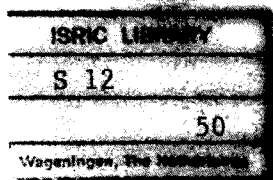
METHODOLOGICAL GUIDELINES
FOR FORECASTING THE GEOCHEMICAL SUSCEPTIBILITY
OF SOILS TO TECHNOGENIC POLLUTION
(Draft)

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INTERNATIONAL SOIL REFERENCE AND INFORMATION CENTRE



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by
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1. ELEMENTAL COMPOSITION OF GLOBAL TECHNOGENIC SUBSTANCE FLOWS AND MODULES OF TECHNOGENIC PRESSURE

1.1 Technogenesis, main concepts and criteria

Technogenesis is defined as an entity of geochemical and geophysical processes related to human activities that alter the geochemistry of the environment. As a geochemical phenomenon it includes:

1. Extraction of chemical elements from the natural environment.
2. Regrouping of elements, including the transformation of the chemical composition of compounds.
3. Release of pollutants, involved in technogenesis, in the environment.

The third type of process is often "hidden". It includes, for instance, the unexpected release of industrial and urban pollutants into the atmosphere, hydrosphere and pedosphere. The dispersion of technogenic elements in the environment can either be due to accidental or incidental processes. The latter include, for example, the routine application of mineral fertilizers, composts, artificial structure stabilizers and pesticides in agriculture. Besides having favourable effects on agriculture, these chemicals may also affect adversely the functioning of biota and soil systems. The negative consequences of technogenesis can be described in terms of the degree of contamination or pollution of soils, water bodies and the atmosphere.

Calculations of the amounts of chemical elements involved annually in technogenic flows, have revealed increased concentrations for a number of elements which do not occur commonly in the biosphere. This means that the 'original' ratios between pairs of elements in the biosphere have changed in recent times. This means that the geochemical environment is becoming less 'comfortable' for biota.

Perel'man (1975) introduced the concept of "technophylity of an element" as a parameter for the technogenic utilization of this element. The technophylity of an element is defined as the ratio of the annual output of the element and its "base level" concentration in the lithosphere.

Often, it is difficult to calculate the "technophylity index". Generally, little is known about the total amounts of elements that are involved in technogenesis alongside the main mineral resources. Moreover, the lithosphere is not the only possible source of chemical elements for technogenesis. Other sources include the atmosphere, for instance as basis for the production of nitrogen fertilizers, and hydrosphere in case of the extraction of salts from seas, oceans and lakes. In view of the above it seems more justified to compare the amounts of chemical elements involved in technogenesis with the corresponding "base level" concentrations in the biosphere. Glazovskiy (1976 and 1982) proposed five indices for calculating the degree of "technogenic utilization" of elements. These indices are enumerated below.

- 1) Coefficient of special technogenic utilization or "special technogeneity" (T_1):

$$T_1 = \frac{M_1 + F_1}{N_n}$$

with:

M_1 the amount of the element (tons) that is mobilized annually (e.g. from an ore deposit) to extract the relevant element or its derivatives.

F_1 the amount of the element (tons) as extracted annually from natural flows (e.g. natural waters) through technogenesis to obtain the specified element.

N_n the "base level" concentration of the considered element in the biosphere.

- 2) Coefficient of total technogenic utilization of the element or "total technogeneity" (T_2):

$$T_2 = \frac{M_1 + M_2 + F_1 + F_2}{N_n}$$

with M_2 and F_2 the quantities of the specified elements that are involved as by-products in the technogenic migration of the "solid" materials and "liquid" flows, respectively.

The coefficients of special and total technogeneity of selected elements are presented in Table 1. They permit to evaluate the respective contributions of individual elements to transformations of the geochemical status of the biosphere. Elements with a high total technogeneity are especially active in the above processes. The latter are often by-products of the mining industry, and as such are quickly dispersed with technogenic flows. Under "natural" conditions, many of these "non-purposefully" mined elements have low "base level" concentrations in the biosphere. However, in view of their high coefficients of total technogeneity these elements belong to the most dangerous category of environmental pollutants.

- 3) Coefficient of technogenic recovery (R). This coefficient is defined as the ratio of the special technogeneity (T_1) and total technogeneity (T_2). As such, it is a measure for the amount of an element that is purposefully mined as compared to the total amount of that element that is involved in technogenesis.

$$R = \frac{(M_1 + F_1) \times 100\%}{M_1 + M_2 + F_1 + F_2} = T_1/T_2 \times 100\%$$

A low value for the R -coefficient is indicative for high "losses" of polluting elements to the environment (Table 2).

Comparison of the coefficients of total technogeneity (Table 1) and technogenic recovery rates (Table 2) shows that the most dangerous environmental pollutants are Fe, Be, U, Se, As, N and S. The coefficients of total technogeneity of these elements ranges from 10^8 - 10^{10} , whereas the coefficients of technogenic recovery (R) are smaller than 20%. B, Cd, Mo, F, Br and Co are also very dangerous

for the environment. Their total technogeneity (T_2) ranges from 10^7 to 10^9 and R-coefficients between 20 and 50 per cent.

Table 1. Coefficients of special technogeneity and total technogeneity for selected elements (according to Glazovskiy, 1982).

Order of coefficients	Special technogeneity (T_1)	Total technogeneity (T_2)
10^{11}	-	Au
10^{10}	Au	Ni, Bi, U
10^9	Bi, Pb, Cu, Ag, W, Zr	Cd, W, Pb, Cu, Ag, J Zn, As, Se, Mo, Zr
10^8	Cl, Zn, Ba, Na, Mo, Sn, Cr Ca, N, Fe, P, As, U, S, Mn, J, Ni	Cl, Ba, S, Na, Cr, Sn Ca, P, Fe, Be, B, Ge, F, Ti, Ni
10^7	Se, Br, Hg, F, B, K, Co, Cs	Br, Mn, Hg, Co, V, Ga, F
10^6	U, Mg, Be, Al, Y, Ti	Mg, Li, Al, Ti
10^5	Tl	-
10^4	Sc	-
10^3	Ga	-

Table 2. Coefficients of technogenic recovery (R) for selected elements (in %).

Element	R	Element	R	Element	R	Element	R
Cl	98	Hg	77	B,Co	31	Si	n
Na, Ag, Ba	91	Br	71	Bi	25	V	n
Li, Fe, Pb	88	P	55	K	22	J	n
Sn	87	Mn	54	S	20	Ge	0.8
Ni	86	Mo, F	45	N, As	17	Sc	0.4
Cr, Zn	83	W	43	U, Se	7.1	Ga	0.024
Cu	81	Cd	38	Be	2.1		

n stands for negligible

4) Mean module of technogenic pressure (P_x). P_x is defined as follows:

$$P_x = \frac{M_x}{S}$$

with:

M_x the total amount of element "x" that is involved annually in technogenesis.

S the area of the region under study.

The module of technogenic pressure can serve to analyze the regularities of the technogenic migration of an element at global scale (Table 3). The mean module of technogenic pressure is considered a useful measure for comparing the impact of technogenically supplied chemicals in different geographical regions.

Table 3. Modules of technogenic pressure for selected groups of elements (in kg.km⁻².year⁻¹; according to Glasovskiy, 1982).

Technogenic pressure module (P)	Elements
500-1000	Na, Cl, Ca, Fe
200-500	S
100-200	N, K
50-100	Al
20-50	P
10-20	Ti, Mn
1-10	B, F, MG, Cu, Zn, Zr, Ba, Pb
0.1-1.0	V, Cr, Ni, As, Br, Sr, Mo, Cd, Sn, J, U
0.01-0.1	Be, Se, Co, Ga, Ge, Se, Bi
0.001-0.01	Li, Ag, W, Au, Hg, Tl
0.0001-0.001	Cs

- 5) Coefficient of biospheric concentration (C_{nx}). This coefficient permits comparison of the impact of various industrial products on the geochemical status of the environment. One coefficient has to be calculated for each of the respective elements of these technogenic products (C_x).

$$C_{nx} = \frac{C_x}{N_{nx}}$$

with:

C_x the concentration of the specified element (x) in the product under study (e.g. coal, oil, mineral fertilizers)

N_{nx} the "base level" concentration of element (x) in the biosphere.

The geochemical effects of industrial products can adequately be estimated by adding up the coefficients of biospheric concentration (C_{nx}) for their most technogenous constituent elements:

$$\text{SUM} \frac{C_{nx_i}}{C_{nx1}} = \text{CN} = \frac{C_{x1}}{N_{nx1}}$$

The CN coefficient of elements that have "base level" concentrations of less than 10⁻³ is as follows: 1500 for coal, 20 for oil, 510 for natural gas, up to 1300 for mineral fertilizers, and 200-3000 for precipitates of sewage sludges.

The coefficients of biospheric concentration in technogenic, geochemical flows are a measure for the mean concentration of these elements in the accumulating media, viz. the atmosphere, hydrosphere, and soil environment. They are respectively called the atmo-technogenic (Ca), hydro-technogenic (Ch) and pedo-technogenic (Cs) coefficient of chemical element concentration.

1.2 Technogenic accumulation of microelements and modules of technogenic pressure on the world soil cover

Nriagu and Pacyna (1988) presented quantified estimates for the technogenic flow of heavy metals and other trace elements in the atmosphere, hydrosphere and water bodies, showing the extent of these processes (Table 4). The rate of technogenic accumulation of most microelements exceeds the naturally occurring process of atmospheric deposition. This even holds true when the lowermost estimates are used for the technogenic inputs. This is particularly apparent for lead, a waste product in car exhaust fumes. Large amounts of technogenic microelements - ranging from tens to thousands of tons annually - accumulate in water bodies and soils over the years. Soils are more severely subjected to this type of pollution than the other accumulating media, viz. the hydrosphere and atmosphere. The most active micro-elements are Cr, Cu, Mn and V. However, when the highest possible figures for technogenic flows are considered, three more elements may be added to this list, namely As, Cd and Hg.

Table 4. Global technogenic input of microelements in the atmosphere, hydrosphere and pedosphere (1000 tons/yr).

Sources	As	Cd	Cr	Cu	Hg	Mn
Atmosphere, technogenic	12-25.6	3.1-12.0	7.3-53.6	19.9-50.9	0.9-6.2	10.6-65.9
Atmosphere, natural	7.8	1.0	-	19	6	5-6
Water bodies, technogenic	12-70	2.1-17.0	45-239	35-90	0.3-8.8	109-414
Soils, technogenic	52-112	5.6-38.0	684-1309	541-1367	1.6-15	706-2633

Table 4 (cont.)

Sources	Mo	Ni	Pb	Sb	Se	V	Zn
Atmosphere, technogenic	0.8-5.7	24.1-87.1	288.7-376.0	1.5-5.5	1.8-5.8	30.1-141.9	70.2-193.5
Atmosphere, natural	1.8-21	33-194	97-180	3.9-33	10-72	2.1-21	77-375
Water bodies, technogenic	30-145	106-544	497-1113	4.7-47	6.0-76	43-222	689-2054
Soils, technogenic	87	325	806	40	18	182	1372

Source: Nriagu and Pacyna (1988)

Important sources of micro-elemental pollution in soils are presented in Table 5. They include residues of coal combustion and rest-products of agro-chemicals.

Table 5. Overview of global technogenic pollution by microelements (Nriagu and Pyacyna, 1988).

Sources	Total amount (10 ⁶ tons)	As	Cd	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Zn
Agricultural and food waste	1.5	3	1.5	47.5	20.5	0.75	85	19.5	25.5	14.2	4.5	3.7	12.5	81
Manure	0.2	3.3	0.7	25	47	0.1	95	14	19.5	11.6	0.4	0.9	5.5	235
Forest consumption and waste	1.1	1.6	1.1	10.1	22.7	1.1	61	1.6	12.5	7.4	2.7	1.6	5.5	39
Urban waste	4.4	0.4	4.2	19.3	26.5	0.13	24.5	2.3	6.1	40	0.76	0.33	0.3	59.5
Municipal sewage	2.0	0.12	0.28	6.2	12.4	0.45	7.7	0.2	13.5	5.75	0.12	0.07	0.75	37.5
Organic waste, incl. excreta	2.1	0.12	0.45	0.24	0.32	-	0.35	0.23	1.7	0.81	0.06	0.04	0.43	1.1
Hard waste, incl. scrap	38	0.11	0.04	1.52	4.37	0.04	2.65	0.08	1.67	7.5	0.08	0.09	0.12	10.9
Coal dust and slag	372	21.8	7.2	305	372	2.6	1076.5	44.5	167.5	143.5	12.3	32.5	33.5	298
Fertilizers	16.6	0.01	0.14	20.5	0.31	-	0.48	0.01	0.37	1.35	-	0.06	0.08	0.68
Peat (fertilizers and fuel)	37.5	0.27	0.55	0.11	1.07	0.01	11.6	0.45	17.6	1.5	0.25	0.2	0.9	1.8
Corrosion of metals, chemicals, and pesticides	-	38.5	1.19	457	559	0.68	300	18.8	19.2	292.5	2.4	0.5	1.7	466
Atmospheric fallout	-	13.2	5.3	21.6	25	2.5	26.7	2.3	24	932	24.5	13.7	12.1	92
TOTAL	-	84	21.3	896.5	954.5	8.3	1670	87.5	325	805	25.8	39.5	181.5	1371.5

About 80-90% of the technogenic arsenic and the major part of the technogenic mercury is added to soils with pesticides. Se is a widely used additive in fodder. Consequently, large amounts of selenium are added to soils with cattle and poultry manure. Urban dumps and sludge waters form major sources of Cu, Pb, Hg, Zn and Cd, S and V pollution in soils.

Assuming a regular pattern for the technogenic accumulation of microelements in arable soils, Nriagu and Pacyna (1988) calculated that each hectare of arable land receives about 1 g of Cd and Sb, almost 50 g of Cu, Pb and Cr, and at least 65 g of Zn and Mn per annum. Consequently, present concentrations of heavy metals in cultivated soils are already much higher than in their pristine analogues. This is even the case when the soils do not occur in urban and industrial areas.

The mean modules of technogenic pressure (P) decrease in the following sequence: Mn > Zn > Cu > Cr > Pb > V > Mo,As > Se > Cd > Hg (Table 6). The extremes recorded are 11.6 kg.km⁻².year⁻¹ for Mn and 0.15 kg.km⁻².year⁻¹ for Cd; this corresponds with an order two difference.

Table 6. Mean module of microelements technogenic pressure and pedotechnogenic concentration for the year 1988.

Elements	Total accumulation in soils (10 ³ tons/yr)	Modules of technogenic press (kg/km ² -land/yr)	Mean conc. in soils* (%)	Modules of pedotechnogenic concentration
As	84.0	0.58	5.10 ⁻⁴	116
Cd	21.3	0.15	5.10 ⁻⁵	3000
Cr	896.5	6.22	2.10 ⁻²	311
Cu	954.5	6.33	2.10 ⁻³	3315
Hg	8.3	0.058	1.10 ⁻⁶	58.10 ³
Mn	1670	11.60	8.5.10 ⁻²	3.6
Mo	87.5	0.61	2.10 ⁻⁴	3050
Ni	325.0	2.26	4.10 ⁻³	565
Pb	805.0	5.59	1.10 ⁻³	5590
Se	39.5	0.27	1.10 ⁻⁶	27.10 ⁴
V	181.5	1.25	1.10 ⁻²	125
Zn	1371.5	9.52	5.10 ⁻³	1904

* After Vinogradov

The risk of soil pollution can be assessed by comparing the modules of technogenic pressure with the "base level" concentrations of the relevant elements in the soil environment. The module of pedotechnogenic concentration (PC_{ex}) is defined as the ratio of the technogenic pressure module (Px) of element 'x' and the "base level" concentration of the relevant element in soils (Cx):

$$PC_{ex} = \frac{P_x}{C_x}$$

The module of pedotechnogenic concentration can be used to assess the destructive effects of the constituent elements of technogenic flows in "natural" soil environments. For each element, the severity of these adverse effects may be expressed either as an absolute figure or in terms of relative concentration of the element.

Microelements can be ordered according to their modules of pedotechnogenic concentration. These modules provide a measure for the polluting hazard and destructive geochemical activity of the considered elements:

<u>Elements</u>	<u>Hg>Se</u>	>	<u>Pb,Cu,Mo,Cd,Zn</u>	>	<u>Ni,Cr</u>	>	<u>V,As</u>	>	<u>Mn</u>
PCs values	n.10 ⁶		n.10 ⁴		n.10 ³		1.2.10 ²		3.6

Hg and Se occupy the first place in this sequence. They have extremely low "base level" concentrations in soils (10⁻⁵ - 10⁻⁶) combined with medium modules of technogenic pressure (in the order of g.km⁻².yr⁻¹). However, their relative concentration in technogenic flows are very high (PCs of 10⁶). Cu, Mo, Cd and Zn have PCs of 10⁴, while Ni and Cr have PCs of 10³. Mn is the last element in the above sequence, even though it has the highest module of technogenic pressure. This is so because the mean "base level" concentration of Mn in soils is rather high, i.e. 8.5.10⁻²%. Consequently, Mn is not considered a pollutant at the prevailing levels of technogeneity.

Technogenic emissions of microelements often influence soil conditions at the global level. Soil conditions in a particular region, however, are further affected by the release of microelements at the local level. Technogenous depositions can be observed within a radius of several tens of kilometres from the polluting source. Following air-borne transport, the technogenic constituents will be deposited on the soil and plant cover. As a consequence, the appearance and floral composition of the vegetation can change within the affected zone. Similarly, the concentration of heavy metals and other microelements in the soil will gradually increase.

Technogenically induced changes in the geochemical composition of soils are most pronounced in the rooting zone where the contents of heavy metals are usually 1-2 orders higher than the "natural" geochemical background. For additional information on this subject, the reader is referred to the work of Zvonariet al. (1978), Arzhanova and Yelpatievskiy (1979), Budun (1975), Obukhov (1983), Zhigolovskaya et al. (1982), Yelpatievskiy and Arzhanova (1985), Sayet and Smirnova (1983), Sorokina (1983) and Lukashev and Simutkina (1984).

Polluting elements generated by local industries and traffic get superimposed over the regional, "agricultural" background. The intensity of the "technogenic background" is determined by the land use pattern and use of agro-chemicals in the specified region, both in the past and present.

From the above discussion it follows that the following will be needed to assess the danger that toxic chemicals will pollute soils in a given region:

- modules of technogenic pressure,
- pedotechnogenic concentration of elements with respect to their "base level" concentrations.
- mean "background" concentrations of the elements in the region under study.

1.3 Atmospheric emissions of selected gases and their acidifying derivatives

In recent times, many industrialised countries have reported a decrease in soil fertility. It has been associated with the widespread application of acid loads, including the use of physiologically acid fertilizers in agriculture and forestry, followed by emission of potentially acidifying gases and the subsequent deposition of "acid rains". This topic has been extensively researched (Bulletin of global pollution..., 1983-1987; Monitoring of long-run transfer..., 1987; Acid rains, 1983; Rovinskiy et al., 1984; Riaboshapko, 1983; Izrael, 1984; Assessing soil degradation, 1977; Acidification today and tomorrow, 1982; Problem of soil acidification, 1987; The increasing acidification ..., 1987; FAO, 1983; Guidelines for general assessment, 1988; Acidification in tropical countries, 1988)

Sulphur, nitrogen and carbon oxides, being water soluble, can produce acid rain. Data on the volumes of sulphides, nitrogen oxides, carbon oxide and hard particles as emitted in various parts of the globe are presented in Table 7a. Considerable differences exist in the degree of atmospheric pollution, both at the regional and national level. There is a 2-3 order difference between emissions in the German Federal Republic, and Finland and Portugal respectively. With respect to continents, total atmospheric emissions are highest for Europe and North America, and lowest for South America. The risk of soils being degraded by acid loads is potentially highest in regions subjected to the highest levels of acid deposition.

Table 7a. Outbursts of selected pollutants into the atmosphere (10⁶ Mln ton/yr).

Continents/ countries	Sulphides	Nitrogen oxides	Carbon oxide	Hydrocarbons	Hard particles
German Federal Republic	8.2	2.4	4.7	0.6	1.6
Finland	0.3	0.1	0.2	0.02	0.2
Portugal	0.07	0.03	0.1	0.02	0.06
Europe (total)	21.6	7.7	21.4	2.6	6.7
N. America	18.1	11.3	77.3	9.0	6.0
Asia	7.5	3.3	8.5	3.3	4.3
S. America	0.3	0.7	2.5	0.3	0.4
Oceania and Australia	2.1	0.7	2.4	0.3	0.32
World (total)	110.4	369.5	1423.8	185.6	256.8

2. SOIL VULNERABILITY AND RESPONSE TO TECHNOGENIC POLLUTION BY CHEMICAL ELEMENTS

2.1 "Vulnerability of soils to chemical pollution"; concepts and general criteria

Soil is an open-ended, bio-mineral system which forms an integral part of a more complex natural ecosystem. Soils are connected with the atmosphere and hydrosphere through substance and energy fluxes, and form a "harbour" for plants and biota. This is the reason why the "vulnerability" of a terrestrial system to degradation can be derived from the properties of this system - the so-called, "landscape geochemical" framework - that promote or hinder the development of a particular type of pollution (Glazovskaya, 1972 and 1976). In order to carry out this type of studies, a thorough understanding of the underlying geochemical processes is needed.

Many transport processes in the landscape are regulated by soil properties, such as the buffering capacity. Fluxes of alkaline pollutants may get neutralized in acid soils, whereas acid fluxes may get neutralized in soils with high contents of Ca- or Na-carbonates. This means that soils act as selective filters for specific chemical compounds; they can be compared with chromatographic columns. Unfortunately, it is also this filtering capacity of soils that makes them vulnerable to chemical pollution.

Pollutants will first accumulate in the organic topsoil. This part of the solum is most actively involved in biological processes. Consequently, these pollutants will be readily accessible to crops and organisms (selective uptake mechanism). The latter play a key role in the geochemical processes occurring in the biosphere, and particularly soil environments (Vernadiskiy). Consequently, the role of plants and biota must be accounted for when elaborating criteria for assessing the risk of soil pollution.

The "natural" functions of soils and sediments can only be preserved if the composition/concentration of pollutants in technogenic fluxes do not:

- 1) disrupt the naturally occurring gaseous, concentrational and redox functions in the soil system. These are the very functions that regulate the "self purifying/regenerating" properties of soils, i.e. regulate the chemical and biological breakdown of technogenic substances.
- 2) interfere with the functioning of the "original" trophic/food chains.
- 3) affect the biological production level of the system.
- 4) cause a change in the "information capacity" of the system. In other words, they should not alter the "original, genetic" composition of biota and plants.

As soon as one of the above criteria is no longer fulfilled, the basic (natural) properties of soil systems will start changing, possibly to the extent of getting irreversibly damaged. The level of biological production, and quality of the resultant products, are considered good indicators for "proper functioning", or stability, of soils within ecosystems.

Soil vulnerability should be assessed with respect to well defined categories of pollutants and polluting processes. Internationally, a wide range of technogenic pollutants are being added to soils. These compounds can be grouped according to their adverse effects on soil properties, i.e. with respect to their pedo-chemically and bio-chemically active components.

Pedo-chemically active pollutants alter the overall "chemistry" of the soil environment through their effect on soil reaction (pH) and redox (Eh) conditions. Examples of such substances are mineral acids, alkali substances, carbonates, physiologically-acid salts, as well as gases such as methane and hydrogen sulphide.

Heavy metals such as mercury, arsenic, selenium, lead, cadmium, chromium, nickel, beryllium, vanadium, strontium, barium belong to the category of bio-chemically active compounds. Radionuclides and "heavy" hydrocarbons, such as defoliants, herbicides and pesticides, are also included in this category.

The vulnerability of soils to technogenic pollution can be derived from the following processes:

- 1) Physico-chemical and bio-geochemical alterations of soil properties. Often times, these cause a drop in soil fertility.
- 2) Bio-chemical degradation/transformation of technogenic compounds that the toxicity of their derived products is either increased or decreased.
- 3) Immobilization/fixation of technogenic substances in new compounds which may occur in forms available or non-available to plants.
- 4) Leaching of soluble pollutants, both within and out of the solum.

2.2 Criteria for forecasting the potential vulnerability of soils to pollution by heavy metals

2.2.1 Waterborne transport of trace elements in soils and geochemical barriers

The chemical composition of technogenic fluxes varies with the pH and redox conditions of the medium. Chemical elements in technogenic fluxes can form colloidal solutions. They can also be sorbed by solid particles present in atmospheric emissions. Smelter plants processing "non-ferrous" metals often produce dust particles containing sulphides, sulphates, oxides, metals and arsenites. Evaporates of arsenic, antimony, cadmium and zinc evaporates can also occur in gaseous form in the atmosphere. Following sorption by small drops of water, as occurring in fogs, these compounds can be deposited on the plant and soil cover.

The chemical speciation/mobility of technogenic elements contained in rain drops, will change when the "rainfall" infiltrates into the soil. Extensive research has been carried out to determine the main regularities underlying the transformation, redistribution and accumulation of technogenic pollutants in a wide range of "non-contaminated" and "polluted" soils (Heavy metals ... 1980, Technogenic flows ... 1981; Methodical recommendations ... 1982; Migration of pollutants in soils ... 1986; Razenkova et al., 1984; Sadovnikova and Zyrin, 1985; Landscape-geochemical fundamentals of background monitoring, 1989).

The relationships between pH and redox conditions in soil samples and the chemical speciation of heavy metal compounds, the impact of heavy metals on soil properties, and possibly adverse effects of heavy

metals for plant nutrition have been studied by Zyryn and Chebotareva (1979), Vorobieva and Rudakova (1980), Obukhov et al. (1980), Pervukhina (1983), Gaponiuk and Kremlenkova (1982), Bineyev et al. (1982), Obukhovskaya and Kaplunova (1983). They are also discussed in "Micronutrients and the nutrition status of soils" (1982).

Arzhanova and Yelpat'ievskiy (1979) and Yelpat'ievskiy and Arzhanova (1985) used lysimeters to study the effects of airborne pollution in a "brown forest mountain soil" located in the proximity of a melting plant. Following transport and deposition, the major part of the heavy metals were retained in the uppermost soil horizon which functioned as a "sedimentation mechanical" barrier. The fraction of water soluble microelements that leached out of the upper soil horizons, was shown to account for a greater share of the total amount of microelements than the atmospheric flow. This points at a partial mobilization of heavy metals in the upper horizon. In the soil under consideration, the concentration of water soluble metals increased by 2.4, 2.1, 4.8, 3, and 2.5 times for Cu, Zn, Cd, Mn, and Cd respectively. The latter were either transported as metal-organic complexes, which accounted for 63 to 90% of the soluble fraction, and in colloidal form. The respective quantities and ratios of soluble and non-soluble metals recorded in the soil solution changed considerably during the infiltration process (Table 7b).

Table 7b Intensity and composition of techogenic input of heavy metals to the brown forest soils of Sikhote-Alin' mountains (Yelpat'ievskiy, Arzhanova, 1985).

Medium	Elements, mg/m ² /year, forms of migration											
	Cu		Zn		Pb		Cd		Fe		Mn	
	1	2	1	2	1	2	1	2	1	2	1	2
Flow from the atmosphere	5.1	8.5	32.4	77.4	87.4	383.4	0.86	1.29	12.9	373.1	9.1	12.3
Soil run off at depths:												
2 cm	12.5	0.5	69.3	2.3	49.2	2.3	4.3	0.06	32.6	43.3	27.2	0.4
40 cm	6.6	0.2	15.9	1.7	8.1	0.6	0.94	0.02	14.0	58.4	12.3	0.9
90 cm	2.4	0.05	4.4	0.17	2.7	0.17	0.29	0.006	4.9	4.9	4.7	0.05

1 - soluble forms; 2 - insoluble forms

More than 55% of the water-soluble lead, that was deposited with the precipitation, was retained in the 0 - 2 cm layer, and more than 90% of it in the organic topsoil (0 - 40 cm). The following percentages of heavy metals were mobilized in the 0 - 2 cm layer: Cu - 47.2, Zn - 77, Pb - 85.4, Cd - 77.2, Fe - 56.3 and Mn - 55 percent. These metals further accumulated in the illuvial horizons (40-90 cm). Below 90 cm depth, however, the following percentages of metals were removed: Cu - 19.2, Zn - 6.3, Pb - 5.5, Cd - 6.7, Fe - 15 and Mn - 17.3 percent. The most mobile elements in this experiment were Mn, Fe and Cu, while Pb was the least mobile.

The solubility of trace metals varies with the pH, redox potential and chemical composition of the soil solution. On the basis of this knowledge, Perel'man (1966) proposed a number of "main categories" for the migration of chemical elements in landscapes. This scheme was later revised by Glazovskaya (1976; see table 8). It shows that the solubility and mobility of trace metals changes with the "water migration class" of the soil (see Section 2.2.2). In practice, genetic soil horizons will form selective barriers for technogenic chemicals contained in technogenic fluxes. Consequently, soils can be viewed as matrices of genetic horizons. The respective columns of these matrices correspond with a particular type of "geochemical barrier".

The theory of geochemical barriers of Perel'man's (1975) is widely used in geochemical studies of landscapes. This researcher distinguished three main categories of geochemical barriers, viz.:

- 1) Bio-geochemical barriers, in which a wide range of elements can be sorbed biologically.
- 2) Physico-chemical barriers, in which elements are retained selectively following "oxidative", "gley reductive", "sulphidic reductive", "sulphate-calcareous", alkaline, acid, "evaporate", adsorption and thermodynamic processes
- 3) Mechanical barriers.

Perel'man (1972) mainly developed the above scheme for the zone of "hypergenesis". Soil-geochemical barriers, however, frequently coincide with soil horizons, which each have their peculiar characteristics. Consequently, the scheme of Perel'man' was revised by the author. Some additional criteria, considered useful to characterize soil-geochemical processes, were added to the scheme.

When rain drops first reach the soil surface they are saturated with oxygen. The "initial" pH of the rain can range from 2.5 to 8.5, depending on the amount and nature of the included contaminants. The pH and redox potential of the "rain" will change when it infiltrates into the soil, so that the speciation/solubility of the contaminants will change. If the initial soil pH is higher than the pH of the technogenic flux (e.g. acid rain in calcareous soils), some elements may get precipitated in an alkaline barrier. However, if the soil had been more acid than the technogenic flux an "acid barrier" would have been formed. This "acid" barrier will selectively retain elements poorly soluble in acid environments. Similarly, "gley" and "hydrogen gley" barriers will selectively retain those metals that are "weakly mobile" under reducing conditions.

Redox and pH conditions do vary widely between soils. Nevertheless, certain combinations of pH and Eh can be associated with specific types of "geochemical" fields. Each of these fields will have their peculiar physico-chemical and thermodynamic barriers. The most common combinations of geochemical barriers in soils are listed in Table 9.

Most genetic soil horizons will function as complex of geochemical barriers. Soil horizons with a high organic matter content often act as mechanical barriers for technogenic fluxes. However, they can also form "chemosorptive", organo-mineral barriers. In situations where there is a net upward water flow, "evaporative sedimentative" barriers can also occur. Illuvial horizons (e.g. B, Bh, Bt, Bca) often function as "sorptive" (Cm) and "chemi-sedimentative" barriers. Examples of the latter are "calcareous", "sulphatic" and "hydroxidic" barriers. Illuvial B-horizons, commonly behave as "mechano-sedimentative" barriers. The same applies for "permafrost plinthite" and parent rocks, when impervious.

Table 8. Main classes for the migration of chemical elements in water in landscapes (Modified after Perel'man, 1966).

Acid-alkaline conditions	Typomorphic		Redox conditions	
	water migrants	air migrants	O ₂ - oxydative medium	CO ₂ , partially CH ₄ -reductive medium
Strongly acid	H ⁺ , SO ₄ ²⁻ , Al ³⁺ , Fe ³⁺		1. Sulphate (H ⁺ -SO ₄ ²⁻)	H ₂ S - reductive hydrogen sulphide medium 2. Sulphate sulphidic (H ₂ S - Fe ²⁺)
Acid	H ⁺ - organic acids, HCO ₃ , Fe ²⁺ , Al ³⁺		3. Organo-acid (H ⁺ -Ch ^b)	4. Organo-acid gley (H ⁺ Ch ^b - Fe ²⁺)
Weakly acid	H ⁺ , HCO ₃ , Fe ²⁺		5. Acid (H ⁺) 7. Weakly acid transitional to calcic (H ⁺ - Ca ²⁺)	6. Acid gley (H ⁺ -Fe ²⁺) 8. Weakly acid gley (H ⁺ - Ca ²⁺ Fe ²⁺)
Neutral and weakly alkaline	Ca ²⁺ , Fe ²⁺		9. Calcic (Ca ²⁺)	10. Calcic gley (Ca ²⁺ Fe ²⁺)
Alkaline	Ca ²⁺ , Na ⁺ , Cl ⁻ , Na ⁺ , SO ₄ ²⁻		11. Calcic-sodic (Ca ²⁺ -Na ⁺) 13. Saline (Cl ⁻ , Na ⁺ , SO ₄ ²⁻)	12. Calcic-sodic gley (Ca ²⁺ -Na ⁺ - Fe ²⁺) 14. Saline gley (Na ⁺ - Cl ⁻ - Fe ²⁺) 15. Saline sulphidic (Na ⁺ -H ₂ S)
Strongly alkaline	OH ⁻ , Na ⁺ , HCO ₃ , SiO ₂		16. Soda (Na ⁺ - OH ⁻)	17. Soda gley (Na ⁺ - OH ⁻ - Fe ²⁺) 18. Soda sulphidic (Na - OH-H ₂ S)

Many micro-elements are poorly mobile under reducing conditions. The relevant elements often accumulate in gley horizons which function as "chemi-sedimentative" barriers under these conditions. Alternatively, "evaporative" barriers are commonly observed in arid and subarid regions. These barriers occur at the depths where the solubility product of the chemical compounds is first exceeded.

Table 9. The most widely spread combinations of soil-geochemical barriers

	A-O	A-G	A-S	N-O-E ₁	N-G-E ₁	N-O-E ₂	Al-O-E ₃	Al-S-E ₃
C ₃ -M ₁		+						
C ₃ -M ₂		+						
C ₃ -M ₃	+							
C ₂ -M ₁	+							
C ₂ -M ₂	+				+	+		
C ₁ -M ₁	+	+			+			
C ₁ -M ₂	+	+				+	+	
C ₁ -M ₃	+	+				+	+	
M ₁							+	
M ₂							+	
M ₃			+				+	+

Indices for soil-geochemical barriers:

A = acid

N = neutral and weakly alkaline

Al = alkaline and strongly alkaline

O = oxygen

G = seasonally-gley and gley

S = hydrogen sulphide

E = evaporate, including:

E₁ = seasonal weakly evaporate

E₂ = seasonal evaporate

E₃ = intensively evaporate

C = organic and organomineral, chemisorptive, including:

C₁ = low capacity

C₂ = medium capacity

C₃ = high capacity

M = Mineral sorptive and chemisorptive, including:

M₁ = low capacity

M₂ = medium capacity

M₃ = high capacity

2.2.2 Soil properties influencing the mobility and risk of accumulation of microelements

The chemical composition of the polluting flux, as well as soil properties and regimes basically determine the form a microelement will have in a particular soil. The accumulation rate, mobility and availability of microelements for plants can vary widely from one soil to another, irrespective of the modules of technogenic pressure and pedotechnogenic element concentration.

The soil properties and regimes that have been used to assess the risk that soils will get polluted subsequent to loading with microelements are:

- 1) pH and redox conditions
- 2) Occurrence of carbonates, Fe- and Al-hydroxides, as well as other inorganic substances capable of chemisorption.
- 3) Nature and size of the organic materials, in that they control the mobility and chemisorptivity of microelements.
- 4) Clay content and mineralogy (sorption properties).
- 5) Hydro-thermic regime of the soil.

The valency of many microelements is pH and redox dependent. Consequently, the solubility and toxicity of these elements in soils will be regulated by the prevailing pH and Eh conditions. The latter conditions can be altered by agricultural practices (e.g. liming) and loading with polluting fluxes.

Scherbina (1972) reported five redox facies under "hypergenic" conditions namely, (1) bivalent iron, (2) bi-and trivalent iron, (3) trivalent iron, (4) chromates and vanadates, and (5) tetravalent manganese (Mn^{4+}) oxides. The first three facies occur in a wide range of soils. The fourth facies ($Cr^{6+} - V^{5+}$), however, is mainly observed in freely drained, alkaline deserts soils that have a low humus content (Perel'man, 1972; Kaurichev and Orlov, 1982). The facies of highest Mn oxidation has not been found in soils.

The mobility of many elements varies markedly with the soil's oxidation status. As^{5+} , Se^{6+} and Mo^{6+} , for instance, are highly mobile in an oxidizing environment, yet practically immobile under reducing conditions. Similarly, the mobility of microelements varies with the pH of the soil solution. In non-polluted soils, the pH generally ranges from 3.0-9.5.

For practical reasons, the soils of the world can be grouped into "geochemical" associations based on their pH and redox conditions (Table 10). The type of "geochemical" field can be used as a tool for predicting the (anticipated) mobility of various micro-elements in soils.

In the association of "organo-acid and acid" soils, heavy metals cations (Hg, Cd, Cu and Zn) are highly mobile. The anion Mo, however, is only poorly mobile under these conditions (Table 10). In the association of "acid gley" soils Se, As and V also become immobile, while the overall mobility of the heavy metals ions decreases. There are no easily mobile elements under these conditions. In the association of "neutral and weakly alkaline" soils of the transitional ($H^+ - Ca^{2+}$), calcic (Ca^{2+}) and calcic-sodic ($Ca^{2+} - Na^+$) water migration class most elements will be moderately mobile. Selenium and arsenic also are readily mobile under "alkaline oxidative" conditions. Lead and cobalt are practically immobile under reducing (gley) conditions.

Cu, Zn, Be, Y, Se and Zr are readily sorbed in "complex radicals" and soluble carbonates in strongly alkaline soils, particularly if the soda content of the soil is high. In this form, these elements are highly mobile. In neutral and weakly alkaline soils, however, the above elements will only form moderately mobile compounds.

Table 10. Microelements with high modules of pedotechnogenic concentration mobility in soils providing for different water migration classes

Classes of water migration	Elements: $P_{\alpha} n 10^6 / n 10^4 / n 10^3$		
	Practically immobile	Moderately mobile	Easily mobile
Organo-acid ($H^+ - Ch^{b+}$)	Mo	Se/Co/Ni, Cr	Hg/Cd, Cu, Zn, Pb/Ar, V
Acid (H^+)	Mo	Se/Pb/Co/Ni, Cr, V, As	Hg/Cd, Cu, Zn
Organo-acid and acid gley ($H^+ - Ch^{b+} - Fe^{2+}$)	Se/Mo/As, V	Hg/Cd, Cu, Zn, Pb/Ni, Cr, Cu	-
Weakly acid ($H^+ - Ca^{2+}$)	Pb	Hg/Cd, Cu, Co, Zn/Ni, Cr, V	Se/As
Weakly acid gley ($H^+ - Ca^{2+} - Fe^{2+}$)	Pb, Mo	Se, Hg/Cd, Cu, Zn, Co/Ni, Cr	-
Weakly alkaline calcic ($Ca^{2+} - HCO_3^-$) ($Ca^{2+} - Na^+$)	Pb, Co	Hg/Cd, Cu, Zn/Ni, Cr	Se/Mo/As
Calcic and sodic calcic gley ($Ca^{2+} - Fe^{2+}$) ($Ca^{2+} - Na^+ - Fe^{2+}$)	Pb, Cd, Cu, Zn, Co	Se/Mo/V, As	Hg/Ni
Strongly alkaline soda ($Na^+ - OH^-$)	Pb	-	Hg, Se/Mo/Cu, Zn/As, V
Soda gley $Na^+ - OH^- - Fe^{2+}$	Pb, Cd, Cu, Zn, Co	Se/Mo/V, As	Hg/Ni
Soda gley sulphuric ($Na^+ - OH^- - H_2S$)	Se, Hg/Cu, Pb, Zn, Co, Cu/Ni	Mo/As, V	-

Most elements become less mobile when acid and neutral soils are flooded (reducing conditions). Perel'man (1972) distinguished two types of naturally occurring reducing media which are referred to respectively as "less reductive - gley" and "strongly reductive - hydrogen sulphide".

Technogenic fluxes generally contain a wide range of sulphur compounds. In freely aerated soils, the sulphur is oxidized to its six-valent form, forming metal-sulphates that are soluble except for barium sulphate. Hydrogen sulphide will be formed when the sulphur compounds reaches a reduced soil layer. Similarly, the chalcophilous elements will be reduced to their bivalent forms, forming non-soluble sulphides or weakly soluble hydrosulphides with metals (e.g. Cu, Zn, Pb, Co, Ni, and Hg). Those elements that are mobile under both "aerated" and "gley" conditions will be immobilized in a hydrogen sulphide medium. The latter phenomenon is commonly observed in poorly drained, saline soils with high contents of sodium and calcium sulphates. Under these conditions, a water soluble complex of mercury-sodium and sulphide will be formed. In saline soils with an "exudative" moisture regime, soluble mercury compounds as well as other salts can be formed in reducing soil horizons. In the uppermost horizons, however, mercury may turn into the stable cinnabar (HgS) upon oxidation of the sulphides.

Soluble Na-borates may accumulate in alkaline saline soils. In acid soils, however, boron will not be very mobile because it is sorbed by iron and especially aluminium hydroxides.

In poorly drained, humus rich, alkaline soils many elements can be sorbed in organo-metallic complexes, forming toxic products. Complexes of mercury and organic compounds are extremely toxic. Since the microbiological activity is suppressed under reduced conditions, these complexes will be very stable. Particularly poisonous forms of methylated mercury have been observed in irrigated rice fields in Japan. Many microelements are sorbed by peat soils. Higher than "normal" concentrations of uranium have been reported for some "humus-gley" soil.

From the above discussions it follows that more than one type of "landscape-geochemical" barrier may occur in a soil under reducing soil moisture regimes, namely "gley", "sulphide", "sorptive" and "biochemical" barriers. Consequently, technogenic elements may occur in various forms under these conditions. Some of these will be mobile and highly toxic.

The repercussions of pollution with heavy metals are likely to be most severe in alkaline hydromorphic soils. Under these conditions, many of these elements will be highly mobile and toxic. Large amounts of toxic precipitates may be formed upon evaporation.

A wide variety of complex, toxic technogenic compounds may occur in geochemical associations comprising soils with seasonally fluctuating redox regimes. Under these conditions, the mobility of each compound will vary with the seasons.

A group of moderately mobile microelements can be distinguished in most acidic, alkaline and redox soil systems. Generally, these elements are not easily leached out of the solum. They tend to accumulate in humus or illuvial horizons and often partake in the nutrient and biological cycle. The group under review comprises elements that can be retained by "sorptive mineral" (Cm) barriers, i.e. be sorbed by colloids, as well as by "organo-mineral" (Ch) barriers. The sorptive capacity of above type of barriers varies with soil texture and mineralogy, and nature of the organic materials in the relevant horizon. The sorption capacity of clay minerals decreases in the sequence allophane > montmorillonite > smectite > kaolinite. Zn, Mn, Cu are preferentially sorbed by allophane, and Ni, Cu, V, Pb and Zn by clay minerals.

Humic acids are very prone to form weakly mobile complexes with metals, particularly with Cr, Co, V, Se and Mo (Stepanova, 1976; Tkachenko et al. 1978; Saprykin, 1984). Complexes of metals and fulvic acids, however, are even more mobile. The sorptive properties and stability of organo-metallic complexes vary with the pH of the medium. The highest values are observed at high pH values. In one study, the average ratio of sorbed zinc over water-soluble zinc was 24 in podzolic soils against 2400 for chernozems. Concentrations of moderately mobile forms of microelements were higher in the illuvial horizon of acid soils (e.g. podzolic soils and soils lessives) than in the humus horizons of the neutral chernozems.

In some soils, microelements may accumulate in weakly mobile forms upon co-precipitation with iron and aluminium oxides. In amorphous ferruginated neo-formations of low moor, for instance, the

concentrations of As, Mn, Zn, Se, Co and Ti were 1-2 orders higher than the corresponding "base level" concentrations in the lithosphere (Taisayev, 1981).

Summarizing, it can be stated a high content in clay minerals - particularly montmorillonite and allophanes -, amorphous oxides of aluminum and iron, organic acids - particularly the humic ones - and a neutral soil reaction will promote the accumulation of moderately mobile forms of microelements in soils. Consequently, the above properties must be accounted for when developing a procedure for estimating the risk that microelements may accumulate in weakly mobile and toxic forms in the pedosphere. It should also be realized, however, that some microelements may get sorbed or bounded in organo-mineral complexes upon application of organic fertilizers, composts and lime, i.e. following a change in land use.

Microelements occurring in hardly mobile forms in soils, generally will not be (very) toxic to biota. These "hardly mobile" compounds are often produced following exchange reactions with carbonates, phosphates (e.g. Pb, Zn, Mo) and sulphates (e.g. Sr, Ba) (Vorobieva et al., 1980).

Some elements may also get immobilized subsequent to isomorphic substitution in the lattices of clay minerals. About 15% of the microelements were found to be isomorphically substituted in a Transcaucasian krasnozem, while it was about 30% in a brown forest soil. Isomorphic substitution of heavy metal ions is a preferential process: $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$. The possible degree of isomorphic substitution also varies with clay mineralogy; it gradually increases in the sequence montmorillonite, nontronite, kaolinite, halloysite and illite.

The hydrothermic regime of the soil also strongly influences the mobility of microelements and as such whether they will accumulate in or leach out of the soil. In humid climates, with net downward water fluxes, water soluble elements are readily leached out of the profile. In soils of subhumid regions possessing an "impermeable" regime, water soluble elements may be precipitated upon "evaporative" concentration. Inherently, these elements will become mobile again upon wetting.

Microelements, mobile under reducing conditions, will continue to accumulate in soils parallel with the loading with technogenic fluxes; the risk of soil pollution will gradually increase under these circumstances. This risk will be even greater for soils having a "stagnant-exudative" water regime, because the microelements that are easily mobile under "water saturated" conditions may form precipitates upon evaporative concentration.

2.3 Criteria for assessing the sensitivity of soils to technogenic acidification

The vulnerability of a soil to acid deposition is determined by the intensity and duration of the acidifying flux, as well as by its initial buffering capacity. The latter capacity can be derived from a titration curve. The effects of technogenic acidification on the buffering capacity of soils have been studied by a wide range of researchers (Tanaka, 1968; Tamm, 1976; Brinkman, 1977; Tamm et al. 1977; Tamm and Wiklander, 1980; Effect of acid precipitation on terrestrial ecosystem, 1980, Ulrich, 1981; Loucks, 1982; Kauppi et al. 1984; Murakyo and Redl, 1987; Tamm and Hallbacken, 1988; Glatzel et al., 1988; Gobrand and Bosota, 1988;

Acidification in tropical countries, 1988, Anderssen and Segman, 1989; Stefanovits, 1989; Patil and Sarwa, 1989). Varallyay et al. (1989) showed that the buffering capacity for acid loads of Hungarian soils is mainly determined by the "initial" soil reaction (pH-H₂O and pH-KCl), content of CaCO₃, hydrolytic acidity, cation exchange capacity, humus content, percentage of exchangeable bases and Al respectively, size of the fine earth fraction, and soil texture.

Statistical analyses of the experimental data in conjunction with the interpretation of titration curves revealed the following relationships between the "buffering capacity" rate (delta-pH; decrease in initial soil pH upon addition of a known amount of acid) and selected soil properties. In the experiments, the soil samples were treated with HCl solutions with concentrations similar to that of "acid rain". The following empirical equations were developed:

HCl mmol	Observed decrease in pH (delta-pH) as compared to the initial pH of the soil sample	
0.1	delta-pH = 1.8 - 0.2E	(r _E ² = 0.737)
0.2	delta-pH = 3.1 - 0.05E - 0.01H	(r _E ² = 0.855; r _H ² = 0.916)
0.5	delta-pH = 3.9 - 0.07C	(r _C ² = 0.914)
1.0	delta-pH = 4.2 - 0.08C + 0.01G	(r _C ² = 0.900; r _G ² = 0.954)

with:

- E the organic matter content (%)
- H the content of clay fraction (%)
- C the hydrolytic acidity (me)
- G the content of silt fraction (%).

According to Stefanovits (1989), the soil buffering capacity is not only determined by the total clay content, but also by the mineralogy of the clay size minerals (e.g. illite, smectite, kaolinite, chlorite, vermiculite). Based on the work of Hargitai (1981), Stefanovits (1989) proposed the following equation for soil buffering capacity:

$$EBCS = EBC_A + EBC_H + EBC_C$$

with:

- EBC_S the total buffering capacity of the soil
- EBC_A the buffering capacity that can be attributed to the initial acidity or alkalinity (content of carbonates) of the soil
- EBC_H as above, but for the organic matter
- EBC_C as above, but for the clay size fraction.

Technogenic acidification will have the most severe repercussions in acid and strongly acid soils. The buffering capacity of acid soils is mainly determined by the rate with which acid fluxes remove exchangeable cations from the exchange complex. Soils with a high cation exchange capacity saturated with bases have the highest buffering capacity.

Upon addition of acidifying compounds, the soil pH will first decrease markedly when the amounts of exchangeable bases get depleted. The hydrolytic acidity of the soil solution will increase gradually, while the ion saturation level will diminish. The calcium, magnesium, potassium, sulphate and nitrate ions that are released following the exchange reactions, can now be leached out of the solum depending on the soil water regime. Consequently, the soils may get impoverished in bases. In strongly acid soils, aluminium ions will be gradually released into the soil solution often reaching concentrations toxic for plants and biota.

Upon the acidification of inherently acid soils, organo-mineral compounds may become mobile. The latter applies particularly to permanently or seasonally flooded soils containing significant amounts of easily-reducible iron and manganese compounds. Commonly, toxic concentrations of water soluble iron and aluminium compounds are reported for soils with impeded drainage conditions.

In the humid subtropics and tropics, and seasonally humid tropics there are extensive areas of soils formed on fersiallitic and ferrallitic weathering crusts, or in derived/reworked products (denudation and redeposition). The buffering capacity of these soils is generally low due to the nature of the clay minerals - mainly kaolinite/halloysite, almost no primary silicate clay minerals -, low reserves of bases and low humus content (Acidification in tropical countries..., 1988). These soils generally contain also a wide range of hydroxides of iron, manganese and/or aluminium. Consequently, they often show a variable charge properties. This means that sulphate- and phosphate-anions may be absorbed by the mineral particles in acid media.

Soil acidification can be especially strong under reducing water regimes (e.g. paddy fields), so that the Fe and Al contained in amorphous hydroxides can be mobilized. The resultant concentrations of Fe and Al often are toxic to even resistant plants.

Acidification does not result rapidly declining buffering capacity in calcareous, strongly alkaline and sodic soils, because the latter contain high amounts of (reactive) calcium carbonate. As a result, they have a high buffering capacity for acids. Consequently, the pH will not drop sharply until the reserves of carbonates become exhausted. In some "calcareous" soils, gypsum may be formed upon acidification. The gypsum crystals will accumulate in the upper part of the solum in case the soil moisture regime is "impermeable" or "exudative". Alternatively, the gypsum may be leached out of solum when there is a net downward water flow.

The alkalinity of solonchic soils and solonchaks will decrease upon acidification. Sodium cations sorbed to the exchange complex will be replaced by calcium if the soil is calcareous, and by hydrogen ions if the soil is acid. The addition of acidifying materials is considered favourable for the properties of this group of soils since it will result in lower levels of alkalinity and the solonchic properties will become weaker.

3. PROGNOSTIC WORLD MAPS OF POTENTIAL STABILITY OF SOILS TO CHEMICAL IMPACTS

The global distribution of soils with similar vulnerability to selected categories of technogenic pollutants has been mapped in this study. Two "soil vulnerability maps" have been prepared; the first depicts the "potential risk of soil pollution by microelements" and the second the "susceptibility of soils to acidification" (see Enclosure). To the author's knowledge, it is the first time that this kind of global maps have been prepared. The maps may serve to increase the general awareness with respect to the ever increasing adverse impacts of technogenesis on soils.

3.1 Cartographic base

The 1:60 M World Soil Map, as produced by Glazovskaya and Fridland, served as the topographical basis for the prognostic maps. This soil map was prepared using the "polyconic" projection as developed by the Central Research Institute for Geodesia, Aerial Photography and Cartography (TsNIIGAiK). The World Soil Map will be published in the "Atlas of World Natural Resources", a publication of the Institute of Geography (USSR Academy of Sciences, In prep.).

The legend to the above map is mainly presented in tabular form. Soils with similar "moisture regimes" are grouped in the columns. The considered regimes are: "very humid and humid", "moderately-humid and moderately-dry" and "dry and very dry". Within a given "moisture regime", the soils are subsequently grouped according to the "water regime". The following "water regimes" have been considered: 1) "percolative", 2) "percolative with periodical surface or ground water excessive moistening", 3) "stagnant", 4) "periodically non-percolative", 5) "pulsating (alternating non-percolative, stagnant, weakly exudative)", 6) "non-percolative", 7) "exudative" and 8) "strongly non-percolative (superficially-exudative)". Alluvial and coastal soils, subjected to periodical flooding, may occur under a range of "moisture regimes".

Soils with similar "temperature regimes" are listed in the rows of the tabular legend. Three classes are considered, viz. 1) "soils of very cold and cold regions with permafrost", 2) "soils of moderately-cold and temperate regions subjected to seasonal freezing" and 3) "soils of warm and hot regions, with or without a cool season, and not subjected to freezing".

The intersections of the columns and rows on the legend correspond with associations of soils with similar hydro-thermic regime, redox and pH conditions.

Besides the above grouping there is also another one: the 104 soil types and subtypes of the 1:60 M map form 21 genetic groups. The soils of these groups have similar pedogenetic features and consequently display similar properties which are reflected in the names of the genetic groups. The genetic groups can best be correlated with the "family level" of the soil classification system of Glazovskaya (1966, 1972), and with the "order level" of the classification scheme of Fridland (1981).

Soils belonging to a particular family are assigned a unique colour on the map (see Enclosure). Soils of the same typological group, that occur in a given topographical landscape (megaforms), and consequently have similar degree of profile development, are visualized on the map using a scheme of black hatchings. Another kind of hatching is used to map the occurrence of skeletal soils and rock outcrops. Similarly, hatchings are also used to differentiate between soils of mountains, uplands, high denudational plains, and those of sedimentary plains. Black symbols are superimposed on the main colour-codes to provide additional visual information on the composition of the soil cover, for instance the occurrence of pans and various "non-soil formations".

In spite of its small scale, the 1:60 M World Soil Map presents fairly comprehensive information about global soil features and regimes. Consequently, it can be used to compile a range of prognostic "soil-geochemical" maps which show the vulnerability of soils to technogenic fluxes of microelements and acid deposition.

The original soil names and mapping unit symbols of the 1:60 M World Soil Map are given below. Generally, these names have been correlated with the 1:5 M FAO/Unesco Soil Map of the World system (see Appendix I).

3.2 Mapping of the vulnerability of soils to technogenic pollution with trace elements

3.2.1 Grouping of the soils of the world according to their response to microelemental pollution

The properties heavy metals and other microelements, as contained in technogenic flows, will change when passing through soils (e.g. solubility/speciation/mobility/biotoxicity). As observed earlier, the pH and redox conditions strongly influence the way in which the chemical compounds will be transformed in soils (Table 10). Consequently, the highest taxonomical level in a classification scheme for technogenic pollution should consist of "geochemical associations of soils". The latter consist of soils having similar redox and pH features (Glasovskaya, 1966 and 1979). Theoretically, this means that technogenic flows of microelements should "behave" similarly in a given "geochemical association". Soils of the same geochemical association have similar genetic profiles, which function as geo-chemical barriers, thus forming a "family". The characteristics and indices of the respective geochemical barriers are shown in Table 9, and the considered "soil families" in Table 11. "Families" are quite useful tools when compiling small-scale, "soil-geochemical" maps showing the potential danger of soil pollution by microelements.

Table 11. Soil families with similar response to pollution by toxic microelements

Index on prognostic map	Soil families	Indices of soil types (on the soil map) - ingredients of families*	Combinations of barriers**	Index on the prognostic map
1	2	3	4	5
1	Flow-accumulative alumo-ferric humus-rich	Ba, Bo, AJI, AJI ^Γ	A-O/C ₃ -M ₃	a
8	Humus-accumulative non-saturated	TTp, ZI ^{ΓII} , ZI	A-O/C ₂ -M ₁	b
15	Flow- and eluvial-illuvial ferric humus	Πσ ^M Πο ^M Πб Πο Πο ^X Π ^M Πο ^{CT}	A-O/C ₂ -M ₂	c
9	Siallitic non-saturated	ZI ΓpII B ^X B B ^{CT}	A-O/C ₁ -M ₁	d
16	Ferrallitic and weakly ferrallitic non-saturated and differentiated	Ж Φж Φ ЖK° Φ° ΦK	A-O/C ₁ -M ₁	e
20	Siallitic clay-differentiated (lessivated and podzolized)	II II ^X B ^X	A-O/C ₁ -M ₁	d
21	Gley eluvial non-saturated	Γэ ^M Γэ II ^r Γэ ^X Γэ ^{CT}	A-G/C ₃ -M ₁	i
2	Peaty-gley and peaty frozen and seasonally freezing	T ^M TB TH	A-G/C ₂ -M ₁	f
10	Gley non-saturated	Γ ^M Γ ΓT ΓII	A-G/C ₁ -M ₂	h
17	Gley and peaty-gley non-saturated, locally with laterite	ΓII ^{CT} B ^{CT} T ^{CT}	A-G/C ₃ -M ₂	g
7	Boggy solonchakous acid		A-S/M ₂	
11	Humus-accumulative weakly unsaturated and neutral, clay-differentiated	Zx ^M Zx JIC II ЧB ЧII ЧIIK Kч	N-O-E ₁ /C ₂ -M ₂	k
18	Weakly ferrallitic and ferrallitic weakly unsaturated and neutral, locally lessivated	Tp Zx ^{CT} Kp K* KB KB ^{II}	N-O-E ₂ /C ₂ -M ₂	o
3	Gleyed humus-accumulative neutral and weakly alkaline	JII ^M JII JII ^{CT}	N-G-E ₁ /C ₂ -M ₁	l
12	Gleyed weakly alkaline and alkaline differentiated solonetzic and solodized	Cz ^M II ^r Cz CH ^{II} Cz ^{CT} CH ^{CT}	N-G-E ₁ /C ₁ -M ₂	m
4	Vertisols and vertic	Ч ^{CT} ЧC CC	N-O-E ₂ /C ₁ -M ₃	p
13	Humus-accumulative saturated	Ч ^r Ч ^{OB} Ч ^{MI} K K ^{CH}	N-O-E ₂ /C ₂ -M ₂	n
5	Meadow-solonchakous and solonchaks	Cx ^M Cx Cx ^{CT} Tx	Al-S-E ₃ /M ₃	v
14	Low-humus calcareous	Ap Ap ^{II} B ^{II} KcB CB CC _{Kч}	Al-O-E ₃ /M ₃	
19	Low-humus solonetzic and gypsic	KcB ^{CH} CH CB ^r Kб ^{CH} CB ^{CH} C _{Kч} ^{CT}	Al-O-E ₃ /C ₁ -M ₂	q
23	Low-humus ferruginated	Kб Kб ^{II}	Al-O-E ₃ /C ₁ -M ₃	r
6	Humusless desertic stony, frequently gypsic	IIx IIx ^r	Al-O-E ₃ /M ₃	
22	Humusless desertic sandy	IIII IIIIK	Al-O-E ₃ /M ₁	

* Appendix 1,2,3

** Table 9

3.2.2 Contents of the map, its possible uses

The legend of the map consists of two tables. In the first one, soil families are placed in rows according to:

- a) The predominant soil water regime, which determines the potential rate of removal, accumulation or evaporative concentration of the most mobile fraction of microelements.
- b) The "water migration class" and, consequently, soil geochemical association.
- c) The anticipated mobility of the respective microelements under the pH and redox conditions proper to the considered soil family.

The respective "water migration" classes are depicted on the map using "chemical indices" (Table 10). The relative mobility of the respective microelements within a given "water migration" class is shown using the following key:

	moderately mobile elements
immobile elements	-----
	easily mobile elements

The study has been limited to the elements with a coefficient of pedotechnogenic concentration of 10^4 and over. Two examples are given below. In the calcic "water migration" class ($\text{Ca}^{2+} \text{HCO}_3^-$), the mobility of micro-elements is as follows:

Pb Se,As
 Hg,Cd,Cu,Co, Zn

The following sequence applies for the soda class ($\text{Na}^+ - \text{OH}^-$):

Pb Hg,Se,Mo,Cu,Zn,As

Soil families are grouped in the rows on account of the nature of the sorptive, chemosorptive and chemosedimentative barriers that will retain "moderately" and "weakly" mobile elements in the upper horizons, which are most directly subjected to pollution. Soil families with similar pollution risk occur at the intersection of the columns and rows.

The second table on the map lists the combinations of soil-geochemical barriers that are most commonly observed in the soil groups considered in the first table of the legend. The lay-out of the second table is as follows. Possible combinations of "acid", "neutral" and "alkaline" barriers with "oxygen", "gley", "hydrogen sulphide" and "evaporate" barrier are shown in the rows. The columns list the possible combinations of "organic", "organo-mineral" and "mineral sorptive", "chemosorptive" and "chemo-sedimentative" barriers. Common combinations of soil-geochemical barriers are found at the intersections of the columns and rows; they are assigned latin letters in the legend and on the map. This means that each mapping unit will have a unique number (Roman numerals), which indicates the prognostic group, and a letter index

denominating the combinations of soil-geochemical barriers that are most representative for the soils of the prognostic group.

The rate of technogenic pollution may be slowed down by reducing the loading of soils with polluting substances. Alternatively, it is possible to develop procedures to "clean up" polluted soils. This will require a thorough understanding of the processes that regulate the breakdown and transport of pollutants in soil systems. The attached prognostic maps provide general information with respect to the nature of these processes. Therefore, the map may be used to formulate guidelines for soil conservation and "detoxication" activities at global level. Further, it may also be used to formulate broad research priorities relevant to the various regions of the globe. Additionally, the 1:60 M map can be used as the basis for estimating the actual state/risk of technogenic soil pollution. To this avail, it should be superimposed onto a map of chemical loading with microelements.

3.3 Map showing the potential buffering capacity of the soils of the world and their susceptibility to technogenic acidification

3.3.1 Grouping of soils according to their buffering capacity and response to acidification

The following materials have been used to group the soils of the 1:60 M map according to their susceptibility to anthropogenic acidification:

- a) Basic, theoretical studies on the probable relationships between the buffering capacity of soils and their susceptibility to acidification (Ulrich, 1981; Muranyi, 1987; Glasovskaya, 1976).
- b) Results of laboratory experiments in which the degrading effects of acid rain and physiologically acid fertilizers on soil properties were simulated. A wide range of soils, with widely differing initial pH values, texture, clay mineralogy and humus content, were included in these studies (Gobran, 1988; Stefanovits, 1989; Varallyay et al., 1989).
- c) Results of long term (20-50 years) field experiments in which changes in the physico-chemical properties of soils subsequent to addition of physiologically acid fertilizers and/or acid rainfall were measured (Rosen, 1989; Puxbaum et al., 1989; Jacks et al., 1989; Tamm 1976, 1977 and 1978).
- d) The small-scale mapping approach developed to assess the susceptibility of Hungarian soils to acidification (Varallyay et al., 1989).
- e) Information about the "initial" properties of the soils shown on the 1:60 M soil map of the world.

In this study, the soils of the world have been divided into 3 main groups based on their (anticipated) response to acidification. The relevant groups are:

1. "Originally acid soils", in which a further increase in acidity will result in a considerable deterioration of the physico-chemical properties and a decrease in fertility.

2. "Soils with weakly alkaline or neutral A horizons and calcareous B horizons by origin". Upon acidification, the properties of these soils will not be deteriorate as rapidly as those of the soils belonging to group 1.
3. "Soils, originally alkaline-calcareous or strongly alkaline and solonetzic". Acidification will reduce the prevailing alkalinity, thereby improving the properties of these soils.

The soils of the above groups are subsequently grouped according to their contents in acid neutralizing agents, such as carbonates, bases occurring in exchangeable form and bound in organo-mineral compounds. One of the criteria for differentiating subgroups is the "ease" with which products of exchange reactions can be removed from or will accumulate in the uppermost soil horizons.

There is a general lack of data about the effects of acid loads on soil properties. Consequently, it is somewhat difficult to assess how various soils will respond to acidification. Nevertheless, changes in the soil buffering capacity of soils upon acidification have been tentatively derived from the "initial" properties of these soils. This has resulted in the following grouping of soils; the overall characteristics and response to acidification of the soils are described below, using the telegram style.

Groups of soils showing similar vulnerability to acidifying compounds:

1. Soils, strongly acid (pH < 4.7) and acid (pH 4.7 - 5.7) throughout the solum. Response to acidification: decrease in pH, increase of hydrolytic acidity and desaturation, increased mobility of fulvates and hydroxides of iron, aluminium, manganese. Under poorly drained conditions, hydrogen sulphide may be formed.
 - 1.1. Extremely low buffer capacity. Very acid soils, mostly coarse-textured (sandy, coarse-silty-sandy), low humus content, low and very low exchange capacity; strongly unsaturated; poor in iron and aluminium hydroxides and alumino-silicates in the upper horizons. This groups includes well and moderately drained podzols (Πo^M , Πo , Πo^X), podzolized zheltzems and krasnozems (XK^D), as well as podzolized, fersiallitic and ferrallitic soils (Φ^D).
 - 1.2. Low buffering capacity. Acid and strongly acid soils, mainly loamy, with low humus content and very low exchange capacity, highly unsaturated, with low content or even absence of aluminosilicates (except the kaolinite minerals) and high content of mainly crystalline iron, manganese, sometimes aluminium, hydroxides. This group includes the well-drained zheltzems and yellow-brown soils (X), yellow ferrallitic soils (ΦX), red-yellow ferrallitic soils (Φ), and humus ferrallitic soils (Φ^F).
 - 1.3. Rather low buffer capacity. Acid soils of different texture, poor in humus, unsaturated, with a low to medium exchange capacity, iron and aluminium hydroxides in the upper horizons, moderate aluminosilicates content. The following soils belong to this group: dystric eluvial-gley soils (Γ^M , Γ^E , Γ^J), peaty-podzolic-gley soils (Π^F), podzolic soils (Π), dystric-gley tundra soils (Γ^M , Γ), and taiga soils (Γ^M , Γ^T).

1.4. Medium and rather high buffer capacity. Strongly acid and acid soils, frequently stony, highly permeable, with a medium humus content and exchange capacity, low amounts of non-crystalline iron and aluminium oxides, considerable contents of weakly weathered aluminosilicates. The well drained, subalpine and alpine meadow soils (Z^{T^A}), primitive mountain-tundra soils (T_{TP}), raw-humus acid forest soils ($T_{p\pi}$), podburs ($\Pi\delta^M \Pi\delta$), and acid brown forest soils (B^k) belong to this category.

1.5. High buffer capacity. Strongly acid and acid soils, highly permeable, very rich in humus, with a very high exchange capacity, unsaturated, abounding in amorphous and weakly crystalline oxides of iron, aluminium, silica allophanes, with a considerable reserve of easy-to-weather minerals. This group includes the well drained, ochric volcanic ash soils (B_o), andosols (B_a) and humus allitic soils (A_{π}^T).

1.6. Very high buffer capacity. Very acid organic soils with a very high exchange capacity, unsaturated, with varying content of iron and manganese amorphous hydroxides. The group includes the poorly to imperfectly drained, gleyed-peat and peat soils ($T^M T^B T^{CT}$), as well as the acid soils of mangroves and marshes ($M M\Gamma$).

2. Soils with weakly acid upper horizons (pH 5.5 - 6.5) and neutral lower horizons (pH 6.5 - 7.5)

2.1. Extremely low buffer capacity. Weakly acid soils, mainly loamy, with a medium humus content, rather unsaturated with a low content of iron and Aluminium hydroxides and weatherable aluminosilicates. The soils of the group predominantly are moderately well to well drained and include the sod-podzolic soils (Π^A), brown lessive soils (B_{π}), and forest and meadow-forest gley soils (Γ_{π} $\Gamma_{\pi}?$).

2.2. Low buffer capacity. Weakly acid, mainly loamy soils with low humus content and very low exchange capacity, moderately unsaturated, with high amounts of iron and locally aluminium hydroxides mainly crystallized and low amount of easily weatherable aluminosilicates. Mainly moderately well drained, dark red ferrallitic soils (ΦK), red and red-cinnamonic soils (K_{ρ}), red residual ferrallitic soils (K_{ρ}^{Φ}), red-brown soils (K_B) and red-brown residual ferrallitic soils.

2.3. Rather low buffer capacity. Weakly acid, mainly loamy soils with moderate humus content, moderately and weakly unsaturated, with rather low iron hydroxides content, considerable amount of weakly weathered aluminosilicates. Predominantly well drained, brown forest soils (B , B^{CT}), sod-taiga soils (Z_T), pale soils (Π_{π}) and dry-arctic cryogenisols (A_{ρ}).

2.4. Moderate to rather high buffer capacity. Weakly acid and neutral, mainly loamy soils with a considerable humus content, high exchange capacity, weakly unsaturated, rich in slightly weathered aluminosilicates, with moderate iron hydroxides content. Mainly moderately well and poorly drained, chernozem-like prairie soils (Ψ_{π}), reddish-black prairie soils (Ψ_{π}^k), gley forest soils and meadow-forest soils (Γ_{π} , Γ_{π}^{CT}).

- 2.5. High buffer capacity. Weakly acid and neutral organic soils with a very high exchange capacity, medium to weakly unsaturated, locally with high content of amorphous and crystalline iron and manganese hydroxides. This group consists mainly of poorly drained, gley-peat soils and shallow-peaty soils of low moor (T^H , T^{CT}).
3. Soils with a calcareous B horizon, and weakly acid or neutral A horizon and a weakly alkaline in B horizon. Upon acidification, there is a decrease in pH, decreasing base cation saturation, bases, increased mobility of calcium- and iron-humates.
- 3.1. Very low buffer capacity. Neutral sandy soils, with a very low to low humus content and an extremely low exchange capacity. Mainly well drained, desert sandy soils ($\Pi\Pi$) and ferruginated sandy soils ($\Pi\kappa$).
- 3.2. Low buffer capacity. Soils are weakly acid in the A horizons, mostly loamy, with low humus content and exchange capacity, slightly unsaturated, poor ion hydroxides in the upper eluvial horizons, with a rather low aluminosilicates amount. Well to moderately well drained, pale podzolized and solodic soils ($\Pi\Pi^3$), and solods ($C\Delta$, $C\Delta^{CT}$) belong to this group.
- 3.3. Rather low buffer capacity. Soils with weakly acid A horizons and alkaline B horizons. Calcareous, mostly loamy and heavy loamy, with a moderate humus content and exchange capacity, saturated or very slightly unsaturated. This group mainly consists of well drained, sod-calcareous soils or rendzinas ($\Delta\kappa^M$, $\Delta\kappa$, $\Delta\kappa^{CT}$), grey forest soils (Π), and leached chernozems (Ψ_B).
- 3.4. Medium and rather high buffer capacity. Soils are neutral in the A horizon and weakly alkaline in B horizon, predominantly loamy, with a low to medium humus content, well saturated with cation bases, exchange capacity. The category is mainly represented by well drained, typical chernozems (Ψ^T), southern chernozems (Ψ^B), chestnut soils (K), cinnamonic soils (K_{Ψ}) and mountain-meadow-steppe soils (Πc).
- 3.5. High buffer capacity. Neutral and weakly acid soils, heavy loamy and clayey, with moderate and low humus content, high and very high exchange capacity, saturated. Mainly moderately and well drained, chernozem-smonitzas (Ψ^{CT}), black vertisols (ΨC), grey soils (CC), and terra rossas (Tp)
4. Soils with a weakly alkaline A horizon and a strongly alkaline B horizon. Upon acidification, there is decrease of alkalinity, ergo pH lowering.
- 4.3. Rather low buffer capacity. Weakly alkaline soils, loamy sandy or sandy loamy, with a low content of humus and exchange capacity, saturated. This group consists mainly of well drained, reddish-brown soils ($K\delta$), and red-brown residual lateritic soils ($K\delta^{CT}$).
- 4.4. Medium and high buffer capacity. Weakly alkaline, mostly loamy soils with a considerable humus content, saturated, locally with solonetzic properties. Mainly, moderately well drained meadow soils (Πr^M , Πr , Πr^{CT}).

4.5. High buffer capacity. Alkaline and strongly alkaline, mostly loamy soils, humus content and exchange capacity are not high, exchangeable sodium present. Predominantly, well drained chestnut solonetzic soils (K^{CH}), light chestnut and brown semi-desert soils (KcB), including members with solonetzic properties (KcB^{CH}), grey-cinnamon solonetz (CK_{π}^{CH}), and reddish-brown solonetz (KB^C).

4.6. Very high buffer capacity. Strongly alkaline soils, usually loamy and heavy loamy, poor in humus, with medium exchange capacity and exchangeable sodium. Well and moderately drained solonetz (CH, CH_{II}, CH^{CT}) are the dominant soils of this group.

5. Soils calcareous throughout. Upon acidification there is a decrease in the content of calcium carbonate. In sodic solonchaks, there is a decrease in sodium carbonates and bicarbonates content; lowering of alkalinity.

5.5. High buffer capacity. Calcareous and strongly calcareous soils of different texture, low humus content and exchange capacity. Well to excessively drained arctic-desert soils (A_{ρ}), high-mountain desert soils (B_{II}), serozems (C), primitive desert soils (II_{ρ}), stony desert soils (II_{κ}), and stony-gypsic desert soils (II_{Γ}) belong to this group.

5.6. Very high buffer capacity. Calcareous, saline, locally sodic soils; weakly drained soils, often showing reducing water regimes. The category includes solonchaks ($C_{\kappa}^M, C_{\kappa}, C_{\kappa}^{CT}$) and takyrs (T_{κ}).

Alluvial soils (A^M, A, A^{CT}) are difficult to place in the system as used above because their properties and regimes can differ markedly at global level. Therefore, areas of alluvial soils are treated as inclusions, and assigned to adjacent mapping units.

3.3.2 The map and its possible uses

The legend to the map is presented in Table 12. The soils are grouped into columns according to their buffering capacity. The rows are used to differentiate between soils whose initial properties are "calcareous" or "non-calcareous" and have similar pH values and profile pattern, and therefore display a similar response to technogenic acidification.

Soils showing similar susceptibility to acidification, i.e. composing similar "groups of risk", are found at the intersections of the rows and columns and indicated with "soil indices". Generally, these "groups" consist of associations of several soil types; 23 "groupings" have been distinguished on the map. Mapping units showing a similar risk to acidification risk are hatched on the map. The highest density of hatching is used for soils having the highest buffering capacity. This category includes the soils that are considered most resistant to acidification.

Table 12. Groupings of the world soils according to buffer capacity and susceptibility to acidification* (Soil indices taken from the world soil map, scale 1:60.000.000) - the list of indices in the graphs is explained in Appendix 1

Soil buffer capacity, ΔpH	Trends of soil changes due to technogenic acidification			Improvement or slight changes
	Strong degradation	Moderate degradation		
	Acidity or alkalinity of initial soils			
	Acid non-calcareous soils		Calcareous in B horizon	Calcareous throughout the solum
	very acid (pH 4.7) and acid (pH 4.7-5.7)	weakly acid in A hor., neutral in B hor. (pH 5.5-6.5) 6.5-7.5	neutral or alkaline in A hor., weakly alkaline in B hor. (pH 6.5-7.5) 7.5-8.5	weakly alkaline in A hor., strongly alkaline in B hor. (pH 3.5-8.0) 8.5-9.5
very low pH 3.5	1	2	-	-
low pH 3.5-2.5	3	4	5	6
rather low pH 2.5-1.5	7	8	9	10
moderate and above moderate pH 1.5-1.0	11	12	13	14
high pH 1.0	16	17	18	19
very high pH does not decrease	21	-	-	22
				23

The map reveals that vast "soil-geochemical" fields occur across the continents. The soils occurring in a given fields will show similar vulnerability to acidification.

Vast fields of strongly acid and acid soils occur in the humid forest belt of the Earth's temperate zone as well in high rainfall areas occurring at medium to equatorial latitudes. The corresponding soils are highly vulnerable to technogenic acidification. Consequently, the repercussions of acidic deposition will be pronounced these areas.

In the subhumid and subarid zones of the temperate and subtropical belts, "less" acid and neutral soils predominate. Generally, these soils are not prone to acidic degradation, even though they do not have a high buffering capacity.

The savanna soils of the humid tropical and subequatorial belts are quite sensitive to acidification processes. They occur extensively in Africa and South America.

The largest "soil-geochemical" field consists of soils that are "weakly" susceptible to acidification. It includes the soils of the deserts and semi-deserts of Central Asia, South-West Asia and North Africa. The soils of this field form a large continuous belt.

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Appendix I. Map unit symbols and soil names according to the Russian Soil Map (1: 60 M) and their FAO/Unesco equivalents.

Map symbols and names of soils in Russian and their literal translation. Soil map of the World, scale 1:60 M		Synonyms in the FAO Soil map system Soil symbols and names of soils ¹	
<u>Пс^Ж</u>	- Подзолы железистые. Ferric podzols	<u>Pf</u>	Ferric Podzols
<u>По</u>	- Подзолы железисто-гумусовые, часто торфянистые. Ferric-humic podzols, frequently peaty	<u>Ph</u>	Humic Podzols
<u>Пс^М</u>	- Подзолы мерзлотные. Podzols with permafrost	<u>Px</u>	Gelic Podzols ²
<u>Пс^{СТ}</u>	- Подзолы субтропические грунтово-глееватые местами с горизонтом плинхита. Subtropical gleyic podzols, locally with plinthite	<u>Pg</u>	Gleyic subtropical podzols, locally with plinthite ⁺
<u>Пб</u>	- Побурь. Podburs	<u>Bds</u>	Spodi-District Cambisols ³
<u>Пб^М</u>	- Побурь сухомерзлотные. Podburs with dry permafrost	<u>Bds</u>	Spody-Dystric Cryic Cambisols ³ +
<u>Тпр</u>	- Тундровые примитивные. Primitive tundra soils	<u>I</u>	Litosols (Leptosols ³)
<u>Дк</u>	- Дерновые остаточнокорбонатные. Leached rendzinas	<u>E</u>	Rendzinas
<u>Дк^{СТ}</u>	- Дерновые остаточнокорбонатные субтропические. Subtropical leached rendzinas	<u>E</u>	Subtropical Rendzinas
<u>Дк^М</u>	- Перегнойно-мерзлотные карбонатные. Raw-humus cryogenic calcareous soils	<u>Ex</u>	Gelic Rendzinas ⁺
<u>Д^{ГХ}</u>	- Субальпийские и альпийские горнолуговые. Subalpine and alpine meadowmountain soils	<u>U</u>	Rankers, Umbric Leptosols ²
<u>Ва</u>	- Вулканические пепловые (андосоли). Volcanic ash soils	<u>Tv</u>	Vitric Andosols
<u>Во</u>	- Вулканические пепловые охристые. Volcanic ash ochric soils	<u>To</u>	Ochric Andosols
<u>Ал^Г</u>	- Аллитные гумусные. Humus allitic	<u>Ah</u>	Humic Acrisols
<u>Грл</u>	- Грубогумусные лесные кислые. Raw-humus acid forest soils	<u>Bdo</u>	Orti-Dystric Cambisols ³
<u>Дт</u>	- Дерново-таежные. Sod-taiga soils	<u>Bh</u>	Humic Cambisols
<u>Б^К</u>	- Буроземы кислые. Acid brown forest soils	<u>Bd</u>	Dystric Cambisols
<u>Б</u>	- Буроземы типичные. Brown forest soils	<u>Be</u>	Eutric Cambisols
<u>Б^{СТ}</u>	- Буроземы субтропические. Brown forest subtropical soils	<u>Be</u>	Eutric Cambisols
<u>Ж</u>	- Желтоземы и желто-бурые. Zheltizems and yellow-brown soils	<u>Bf</u>	Ferrallitic Cambisols
<u>Фж</u>	- Желтые ферраллитные часто с горизонтом плинхита. Yellow Ferrallitic, locally with plinthite	<u>Fx</u>	Xantic Ferralsols locally with plinthite ⁺
<u>Ф</u>	- Красножелтые ферраллитные местами	<u>Fa</u>	Acric Ferralsols, locally with plinthite ² +

	с горизонтом плинтита. Red-yellow ferrallitic locally with plinthite		
<u>ФК</u>	- Красноземы и темнокрасные ферраллитные. Red and dark red ferrallitic	<u>N, Fr</u>	Nitossols and Rhodic Ferralsols
<u>ФГ</u>	- Ферраллитные гумусные. Humus ferrallitic soils	<u>Fu</u>	Umbric Ferralsols
<u>П</u>	- Подзолистые типичные. Typic podzolic	<u>Dd</u>	Dystric Podzoluvisols
<u>ПГ</u>	- Подзолистые торфянисто-глеевые. Peaty gleyic podzolic	<u>Dg</u>	Gleyic Podzoluvisols
<u>П^л</u>	- Дерново-подзолистые и почвы лессивы. Sod-podzolic and lessivé soils	<u>La</u>	Albic Luvisols ²
<u>Б^л</u>	- Бурные лессивированные. Brown lessivé soils	<u>Bl</u>	Luvic Cambisols ⁺
<u>ЖК^о</u>	- Желтоземы и красноземы оподзоленные. Podzolized zheltozems and krasnozems	<u>Lc</u>	Chromic Luvisols
<u>Ф^о</u>	- ферраллитизированные и ферраллитные оподзоленные часто с горизонтом латерита. Ferrallitized and ferrallitic podzolized, frequently with laterite	<u>Flp</u>	Luvi-Plinthic Ferralsols ^{3 +}
<u>ГЭ^м</u>	- Глееэлювиальные мерзлотные. Gley-eluvial soils with permafrost	<u>Lga</u>	Albi-Gleyic Gelic Luvisols ²
<u>ГЭ</u>	- Глееподзолистые часто торфянистые. Gley-podzolic frequently peaty	<u>Dg</u>	Gleyic Podzoluvisols
<u>ГЭ^п</u>	- Глееэлювиальные дерновые (псевдопели, псевдоподзолистые). Gley-eluvial soddy (pseudogleys, pseudopodzolic)	<u>Lga</u>	Albi-Gleyic Luvisols
<u>ГЭ^{ст}</u>	- Глееэлювиальные субтропические, часто с горизонтом латерита. Gley-eluvial subtropical, frequently with laterite	<u>Lga</u>	Albi-Gleyic Luvisols subtropical, with plinthite ^{3 +}
<u>Г^м</u>	- Глеевые тундровые мерзлотные. Tundra gley soils with permafrost	<u>Gx</u>	Cryic Gleysols
<u>Г^т</u>	- Глеевые таежные мерзлотные. Taiga gley soils with permafrost	<u>Gx</u>	Cryic Gleysols
<u>Г</u>	- Глеевые тундровые. Tundra gley soils	<u>Gd</u>	Dystric Gleysols
<u>Г^т</u>	- Глеевые таежные. Taiga gley soils	<u>Gd</u>	Dystric Gleysols
<u>Г^л</u>	- Глеевые лесные и лугово-лесные. Gley forest and meadow-forest soils	<u>Gh</u>	Humic Gleysols
<u>Г^л</u>	- Глеевые субтропические часто с горизонтом латерита. Gley subtropical soils frequently with laterite	<u>Gp</u>	Plinthic Gleysols
<u>Б^л</u>	- Лугово-болотные субтропические. Meadow-boggy subtropical soils	<u>Ghd</u> <u>Gu</u>	Humi-Dystric Gleysols ³ Umbric Gleysols ²
<u>Т^м</u>	- Торфяно-глеевые и торфяные мерзлотные. Peaty gley and peaty soils with permafrost	<u>Ox</u>	Gelic Histosols
<u>Т^в</u>	- Торфяно-глеевые и торфяные верховых болот. Peaty-gley and peaty soils of high moor	<u>Od</u>	Dystric Histosols
<u>Т^н</u>	- Торфяно-глеевые и торфяные	<u>Oe</u>	Eutric Histosols

	низинных болот. Peaty-gley and peaty soils of low moor		
<u>ТСТ</u>	- Торфяно-глеевые и торфяные субтропические. Peaty-gley and peaty subtropical soils	<u>Oe</u>	Eutric Histosols subtropical ⁺
<u>Ар</u>	- Арктические сухомерзлотные. Arctic soils with dry permafrost	<u>Rx</u>	Cryic Regosols
<u>Пл</u>	- Палевые. Pale soils	<u>Lk</u>	Calcic (Cryic) Luvisols ⁺
<u>Пл³</u>	- Палевые оподзоленные, осолоделые. Pale podzolic, solodized soils	<u>Lx</u>	Cryic Luvisols ⁺
<u>П</u>	- Серые лесные. Grey forest soils	<u>HI</u>	Luvic Phaeozems
<u>ЦВ</u>	- Черноземы выщелоченные и оподзоленные. Leached and podzolized chernozems	<u>Cl</u>	Luvic Chernozems
<u>АМ</u>	- Аллювиальные мерзлотные. Alluvial with permafrost	<u>Jx</u>	Cryic Fluvisols
<u>М</u>	- Маршевые болотные и солончаковые. Marshy boggy and solonchakous soils	<u>Gt</u>	Thionic and solonchakous Gleysols
<u>А</u>	- Аллювиальные. Alluvial soils	<u>J</u>	Fluvisols
<u>АСТ</u>	- Аллювиальные субтропические. Alluvial subtropical soils.	<u>J</u>	Fluvisols
<u>Мг</u>	- Мангровые болотные и солончаковые в том числе кислые. Mangrove boggy and solonchakous soils, acid soils included	<u>Gt</u>	Thionic Gleysols ²
<u>Тк</u>	- Такыры и такыровидные. Takyrts and takyr-like soils	<u>Yt</u>	Takiric Yermosols ⁺
<u>Лг</u>	- Луговые, местами солончаковатые, солонцеватые и осолоделые. Meadow, including solonchakous, solonetzic, planosolic (solodic)	<u>Gu</u>	Umbric Gleysols, locally solonchakous, solonetzic, planosolic
<u>СНП</u>	- Солонцы луговые часто осолоделые. Meadow including solonchakous, solonetzic, solodic	<u>Sg</u>	Gleyic solonetztes, frequently planosolic
<u>СНСТ</u>	- Солонцы субтропические. Subtropical solonetztes	<u>S</u>	Subtropical solonetztes ⁺
<u>ЛгСТ</u>	- Луговые субтропические преимущественно слитые, местами осолоделые. Meadow subtropical, locally solodic, mainly vertic	<u>Gmv</u>	Verti-Mollic-Gleysols, locally planosolic ^{3 +}
<u>Лс</u>	- Лугово-степные, субальпийские и альпийские местами мерзлотные. Meadow-steppe subalpine and alpine, locally cryogenic	<u>Im</u>	Mollic Leptosols locally cryogenic ²
<u>Сд</u>	- Солоды (планосоли). Solods (Planosols)	<u>W</u>	Planosols
<u>СдСТ</u>	- Солоды (планосоли) субтропические. Subtropical solods (Planosols)	<u>W</u>	Planosols
<u>ЦГ</u>	- Черноземы типичные. Typical chernozems	<u>Ch</u>	Haplic Chernozems
<u>ЦОЮ</u>	- Черноземы обыкновенные и южные. Ordinary and southern chernozems	<u>Ck</u>	Calcic Chernozems
<u>ЦМЦ</u>	- Черноземы глубокие мнцеллярно-карбонатные. Deep Chernozems with mycelium carbonates	<u>Ck</u>	Deep Calcic Chernozems ^{2 +}

<u>К</u>	- Темно-каштановые и каштановые. Dark chestnut and chestnut soils	<u>Kh</u>	Haplic Kastanozem
<u>К^{CH}</u>	- Темно-каштановые и каштановые часто солонцеватые. Dark chestnut and chestnut soils frequently solonetzic	<u>Kl</u>	Luvic (solonetzic) Kastanozems ⁺
<u>Кч</u>	- Коричневые сухих лесов и кустарников. Cinnamonic soils of xerophylous forests and shrubs	<u>Bc</u>	Chromic Cambisols
<u>Ч^{CT}</u>	- Черноземы субтропические (Черноземы смолницы, terra negro). Subtropical Chernozems (Smolnitza)	<u>Chv</u>	Vertic Chernozem = Veg Grumi-Eutric Vertisols
<u>Чп</u>	- Черноземовидные почвы прерий, местами глееватые и осолоделые	<u>Hh</u>	Haplic Phaeozems, locally gleyic and sodic ⁺
<u>Чпк</u>	- Черноземовидные и красновато-черные почвы прерий, местами глееватые и осолоделые	<u>Hh + Hhc</u>	Haplic Phaeozems and Chromi-haplic Phaeozems, locally gleyic and sodic ⁺
<u>Тр</u>	- Terra rossa	<u>E</u>	Terra Rossa
<u>Кр</u>	- Красные и красно-коричневые	<u>Nr, No</u>	Rhodic and Haplic Nitosols ²
<u>КБ</u>	- Краснобурные и бурные	<u>Bc</u>	Chromic Cambisols ²
<u>КБ^Ф</u>	- Краснобурные остаточо-ферраллитные	<u>Bcf</u>	Ferrallic chromic Cambisols ^{3 +}
<u>Пф</u>	- Песчаные ферраллитизированные	<u>Qf</u>	Ferrallic Arenosols
<u>Л^{ГМ}</u>	- Луговые мерзлотные солонцеватые и осолоделые	<u>Gmx</u>	Mollic gelic Gleysols ³
<u>С^{дМ}</u>	- Солоди и осолоделые солонцы мерзлотные	<u>Wis</u>	Si Solodic gelic Planosols and gelic Solonetztes
<u>ЧС</u>	- Темноцветные слитые. Dark vertic soils	<u>Vp</u>	Pellic Vertisols
<u>СС</u>	- Серые, часто солонцеватые осолоделые и глеевые	<u>Vk</u>	Calcic Vertisols, frequently solonetzic, planosolic, gleyic ^{3 +}
<u>С^{кМ}</u>	- солончаки мерзлотные. Solonchaks with permafrost	<u>Zi</u>	Gelic Solonchaks
<u>Ск</u>	- солончаки. Solonchaks	<u>Z</u>	Solonchaks
<u>С^{кCT}</u>	- солончаки субтропические. Subtropical Solonchaks	<u>Z</u>	Solonchaks
<u>Ар^{II}</u>	- Арктические пустынные. Arctic desert	<u>Rx</u>	Gelic Regosols
<u>В^{II}</u>	- Высокогорные пустынные. Arctic desert	<u>Ie</u>	Eutric Leptosols ²
<u>КсБ</u>	- Светлокаштановые и бурные пустынно-степные. Light chestnut and brown desert-steppe soils	<u>Xh</u>	Haplic Xerosols
<u>СБ</u>	- Серо-бурные пустынные. Grey-brown desert soils	<u>Yl</u>	Luvic Yermosols
<u>С</u>	- Сероземы. Serozems	<u>Xk</u>	Calcic Xerosols
<u>СКч</u>	- Серокоричневые. Grey cinnamonic	<u>Bk</u>	Calcic Cambisols
<u>Кб</u>	- Красновато-бурные. Reddish-brown	<u>Bcc</u>	Calcari-Chromic Cambisols ²
<u>Кб^{ЛТ}</u>	- Красновато-бурные остаточо-латеритные. Reddish-brown residually lateritic	<u>Bcc(p)</u>	Calcari-Chromic Cambisols with plinthite
<u>Ппр</u>	- Пустынные примитивные. Desert primitive soils	<u>Rc</u>	Calcaric Regosols = Yi Leptic Yermosols ⁺

<u>КсБ^{СН}</u>	- Светлокаштановые и бурые пустынно-степные солонцеватые. Light-chestnut and brown desert-steppe solonetzic	<u>Xk</u>	Calciic solonetzic Xerosols ⁺
<u>Сн</u>	- Солонцы. Solonetztes	<u>S</u>	Solonetztes
<u>СБ^Г</u>	- Серо-бурные гипсоносные и солончаковатые. Grey-brown gypsic and solonchakous soils	<u>Y</u>	Gypsic luvic Yermosols
<u>СКч^{СН}</u>	- Серо-коричневые солонцеватые и гипсоносные. Grey-cinnamonic solonetzic and gypsic	<u>Bks</u>	Calciic Cambisols, solonetzic and gypsic ⁺
<u>Пп</u>	- Песчаные пустынные. Sandy desert soils	<u>Qc</u>	Calciic Arenosols ²
<u>Ппж</u>	- Песчаные пустынные ожелезненные. Sandy desert ferruginated soils	<u>Qcf</u>	Ferry-calcaric Arenosols ³
<u>Пк</u>	- Пустынные каменистые. Desert stony soils	<u>Rc</u>	Calcaric Regosols
<u>Пк^Г</u>	- Пустынные каменистые гипсоносные. Desert stony gypsic soils	<u>Rcy</u>	Gypsi-calcaric Regosols ³

+ with additions, not always in terms of FAO legend

Appendix II.

Appendix III. List of geochemical barriers.

SOIL-GEOCHEMICAL BARRIERS

Combination of sorptive barriers	Combination of acid-alkaline and oxygen-reducing barriers							
	A-O	S-G	A-S	N-OE ₁	N-O-E ₂	N-G-E ₁	Al-O-E ₃	Al-S-E ₃
C ₃ -M ₁		f						
C ₃ -M ₂		g						
C ₃ -M ₃	a							
C ₂ -M ₁	b					e		
C ₂ -M ₂	c			k	n			
C ₁ -M ₁	d	h				m		
C ₁ -M ₂	e	i			o		q	
C ₁ -M ₃					p		r	
M ₁							s	
M ₂			j				t	
M ₃							w	v

Indices of soil-geochemical barriers

A = acid

N = neutral and weakly alkaline

O = oxygen

G = gleyic

S = reducing hydrogen sulphide

E = evaporative

E₂ = seasonal strong

E₃ = strong

E₁ = seasonal weak

C = organic and organosorbative, chemisorptive

M = mineral sorptive and chemosedimentive; for sorptive barriers

M₃ = high capacity

M₂ = medium capacity

M₁ = low capacity

