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Review

Surface Water under Growing Anthropogenic Loads: from Global Loads to Regional Consequences: A Review

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Abstract: The paper presents a review of currently available evaluations of the effects of continuously increasing anthropogenic loads on water resources. The increase in the fluxes of elements and compounds into the environment, such as the emission of greenhouse gases and dispersion of nutrients (nitrogen and phosphorus), acidifying gases, and toxic elements and compounds that adversely affect the water quality are considered. The significance of fresh waters as a life support factor of the human populations is demonstrated. Examples are presented to illustrate how key anthropogenic induced processes develop in land waters under the effect of anthropogenic loads, as exemplified by the Russian Kola regions. Climate warming and the increasing dispersion of elements are demonstrated to result in the eutrophication of surface waters even in areas remote from anthropogenic impacted regions. Although the emissions of acidifying gases diminish, the waters are still acidified in acid-vulnerable areas, and the chemical compositions of the waters have been significantly modified over the past decades, which indicates that the changes in the chemical composition of the waters are of irreversible. A new feature of the waters is distinguished: the toxicity of the habitats for aquatic organisms. Arguments are presented for establishing a theoretical approach for evaluating critical loads.

Keywords: surface water; anthropogenic loads; warming climate; eutrophication; acidification; critical loads

1. Introduction

The explosive growth of the human population, the intense development of mineral resources, and technological progress in the 20th century dramatically affected the environment, as had become obvious by the mid-20th century. V.I. Vernadsky [1] stressed that human activities can fundamentally and rapidly modify both many natural processes and what is referred to as laws of nature.

The paramount significance of fresh waters for the human population our planet and for preserving the species diversity on Earth demonstrate how important to study water resources affected by ever growing anthropogenic loads. The transformations of catchment, airborne pollution, the discharge of industrial wastes and domestic sewage, and diffuse runoffs contaminate aquatic systems and change the biogeochemical cycles of elements in the systems of catchments and water bodies, lead to the acidification, eutrophication of the lakes and rivers, and bring toxic compounds into the waters. These processes eventually downgrade the quality of the waters and diminish the biological diversity of the aquatic systems. The withdrawal of the runoff and climate warming are also reflected in changes in the hydrogeological cycles and fluxes of elements from catchments to lakes and rivers [2,3]. It is hard to understand all direct and indirect consequences of anthropogenic impacts onto water resources, and hence, below we will focus mainly on the following problems (Figure 1):

- the use of water resources as a life necessities on the planet;
- the effect of climate warming on the eutrophication of waters;
- the consequences of acidic deposition for the water acidification;

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- the transfer of toxic elements and compounds to natural waters;
- principal theoretical approaches to the evaluation of critical loads.

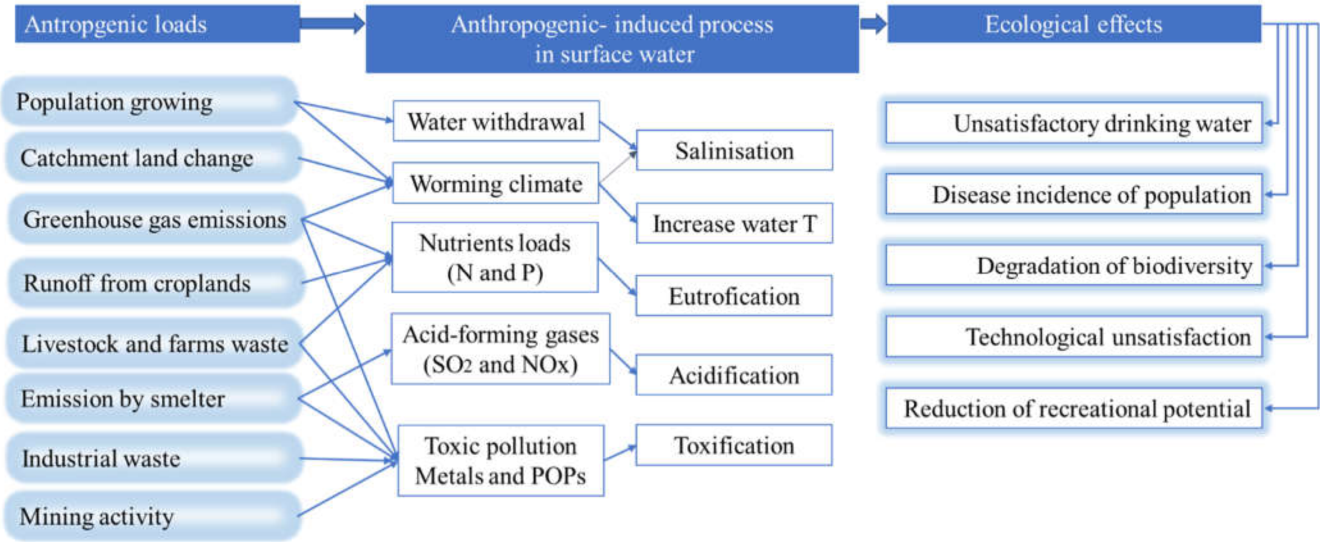

Figure 1. Flowchart showing anthropogenic loads on surface water and its consequences.

Analysis of currently available estimations of the quality of natural surface waters in the Arctic basin shows that this territory is still studied inadequately poorly. The north-eastern part of the Scandinavia shield (northern Kola Peninsula) has been impacted by anthropogenic loads for more than eight decades, and the local waters are susceptible to all anthropogenic loads because of the sluggish material and energy exchange in the cold latitudes. Below we employ this region is as an illustrative example to discuss, based on results of our long-term studies in the area [4-10], how anthropogenic induced processes evolve in the surface waters. In natural environments, the waters of the region are low total dissolve salt (TDS) and are poor in biogenic elements (nutrients). In their pristine natural state, lakes in the Arctic basin are ultrafresh and oligotrophic. Note that these water chemistry, as and anthropogenic loads, typical of numerous lakes in the Arctic zone of our Planet.

2. The importance of freshwater in the life support

The worldwide utilization of freshwaters is evaluated at 2,600 km^3 per year and was 415 km^3 per year in the preindustrial epoch [11]. Nowadays approximately 70% of the world's freshwater resources is used for agricultural needs, 20% is utilized by industries, and 10% is consumed for domestic purposes. According to global evaluations [12], the allowable global water withdrawal threshold has not been exceeded as of yet. The global consumption of freshwater by the humankind amounts to 4,000 km^3 per year.

It should be mentioned that water resources are unevenly distributed over the planet's surface, and much of these resources occur in northern areas that are sparsely populated. For example, the average long-term total runoff of northern rivers is estimated at 4,300 km^3, which is commensurable with the allowable freshwater consumption by the whole world's human population. The northern areas are populated very sparsely. The total volume of secular freshwater resources stored in Russia's lakes is 26,500 km^3. (including 23,000 km^3 in Lake Baikal, 903 km^3 in Ladoga Lake, and 295 km^3 in Onega Lake). The runoff of large Siberian rivers, first of all, Ob, Lena, and Yenisei, amounts to 1600 km^3 per year, i.e., one-third of the world's riverine runoff [13].

The greatest deficit of water resources (not only in terms of quantity but also in the quality of the waters) occurs in densely populated step and arid parts of our planet, in which more than 40% of the world's human population currently lives. Statistical data indicate that practically one-fifth of the global population suffer from an acute shortage

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of drinkable water [14]. According to scientific estimates, more than half of countries worldwide will either have suffered from serious water shortage or its insufficient supply by the year 2025, and already three-fourths of the Earth's population will have been critically short in freshwater for the mid-21st century. According to estimates, 47% of the world's population will have been seriously threatened by water shortage by 2030. The population is going to significantly grow by 2050 in rapidly developing countries, which are already short of water [15].

Along with water deficit, an important problem is the contamination of freshwaters with industrial emissions and discharges, the runoff of fertilizer-contaminated waters from urbanized territories, atmospheric fallouts, and the penetration of salty waters into fresh aquifers in coastal areas because of groundwater withdrawal. Operating along with such global processes as climate warming, anthropogenic loads result in both quantitative and qualitative depletion of water resources.

3. Effect of climate warming on aquatic systems

Lately many researchers worldwide focused on the effects of climate warming. The planet's average air temperature has increased by 1.5^{o}C since 1980, and the Earth's surface continues to warm at a rate of approximately 0.16^{o}C per decade, with this rate varying from one region of the planet to another. It has been proved that the warming of the biosphere brings about to weather instability, along with changes in atmospheric precipitation and disturbances in hydrological cycles (longer arid periods and expansion of deserts in a warm climate with a simultaneous increase in precipitation and flooding in humid zones). The principal reason for climate warming is the ever growing emission of greenhouse gases, first of all, CO_2. The atmosphere now contains 42% more CO_2 than at the beginning of the industrial era [16]. The latest IPCC report shows that emissions of greenhouse gases continue to rise, and current plans to address climate change are not ambitious enough to limit warming to 1.5°C above the preindustrial level [17].

The global warming intensifies biocycling in the freshwater system and facilitates establishing of feedbacks and changes in the environment, landscapes, and the human society. An increase in air temperature, particularly in summertime and early autumn, means that the atmosphere can retain more water [3]. Climate changes also result in that more moisture is brought from lower latitudes to the pole. This increases the amount of precipitation in the Arctic, with this precipitation falling off in the form of either rains or snowfalls. In many parts of the Arctic, the amount of precipitation in the form of rain (but not snow) has increased, and the snow-cover period has become shorter [18].

Climate warming also affects the runoff [19]. An increase in the precipitation, runoff, and ice melting in ice covers results in that greater volumes of freshwater flow into the Arctic Ocean. For example, the riverine runoff was estimated to increase to 4200 km^3 (±420 km^3) in 2000–2010 as compared to 3900 km^3 (±390 km^3) in 1980–2000. It is predicted that these changes should continue, and numerical simulations indicate that the riverine runoff will perhaps increase by 25 to 50% over most of the Arctic [18]. The example of large Siberian rivers, such as Ob (at the gauging section in Salekhard), Yenisei (Igarka), and Lena (Kyusyur), indicates that an increase in the runoff of these rivers was simultaneous with the onset of the modern air warming. It has been demonstrated that the long-lasting phases of runoff changes are synchronous with phases of changes in the air temperature and large-scale atmospheric circulation [20].

The most hazardous phenomenon is that warming impacts permafrost rocks (PFR), which are widespread in continental West Siberia over an integral area of about 700 thousand km^2, i.e., more than one-fifth of the area. The thawing of permafrost peatlands in northern West Siberia may increase the release of methane and other greenhouse gases and augment water volumes in the rivers and lakes. The intensification of the thermokarst process should increase in the number of the lakes and in their surface area [21-24].

The snow cover is the main source of annual runoff water in summertime in northern territories, controls the export dynamics of nutrients, and dissolved organic carbon

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(DOC). Changes in the hydrological cycles should inevitably modify concentrations and removal of chemical elements in the waters, including suspending matter, DOC and nutrients, [25]. Climate warming should change (with regard to the predictions) the time and intensity of snow melting, which in turn, should change the runoff to the lakes and marginal seas. Therewith the frequency of the autumn storms and floods may increase [26]. It is still largely uncertain how these factors may correlate with changes in the transfer of dissolved compounds from the catchments, but it is obvious that the biogeochemical cycles in the catchment–water body system should thereby change.

The literature presents ample evidence that climate changes result in changes in the chemical composition of the waters [27-29]. D. Houle et al. [30] mention that higher annual average air temperatures correlate with the pH of the lake waters in long time series of monitoring data. The increase in the content of organic matter may by explained by the increase in the influx of nutrients (nitrates and phosphates) from the catchments as a consequence of the climate warming [9,31].

The influence of temperature on water resources is controlled primarily through changes in the hydrological conditions under which the waters are formed and through biogeochemical cycles, i.e., the amount of the precipitation, the occurrence of a snow cover, the conditions of the rocks underlying soils at the catchments, the saturation or depletion of the waters with exchange bases and accumulation at the catchment over the historical period, microbiological activity, the acceleration of vegetation growth, and perhaps, also the runoff of nutrients.

It has been demonstrated [6] how an elevated temperature affects the chemical composition of waters in various natural climatic zones (from the Arctic to steppes). These data indicate that temperature most strongly effects on the water eutrophication. Three-parameter dependences were derived for parameters of the chemical composition of the waters on climatic parameters at the catchments. These dependences provided a basis for prognostic models that made it possible to predict the probable changes in salt and phosphorus concentrations in surface waters at warming for 0.5, 1.0, 1.5, and 2.0^{o}C (Figure 2).

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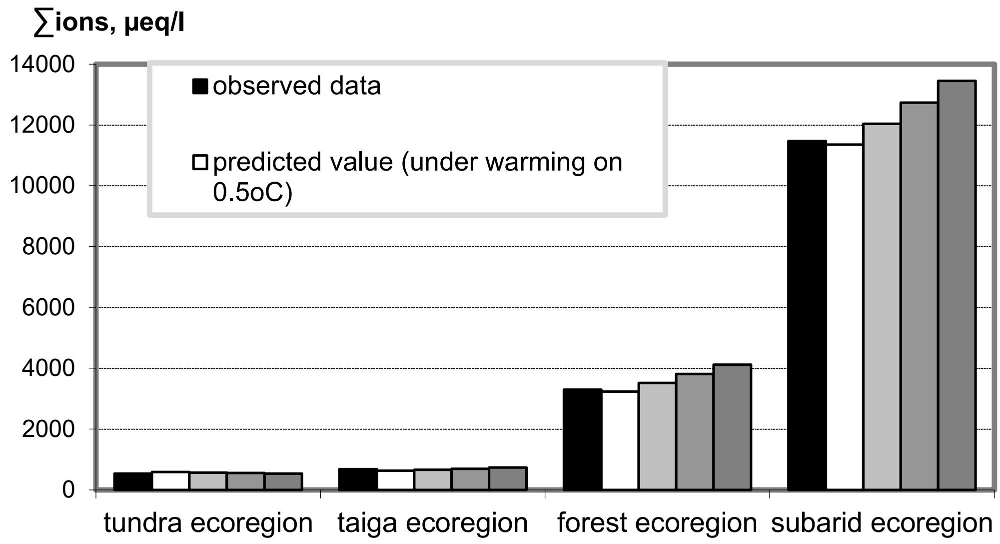
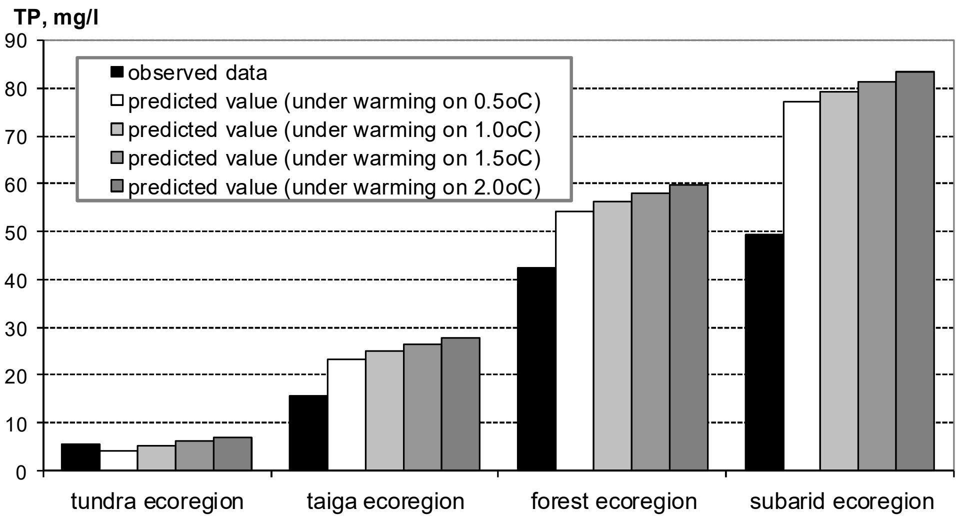


(a)



(b)

Figure 2. The observed and predicted values of sum ions (a) and total phosphorus (b) for the climatic ecoregions within European Russia along a climatic transect from northern tundra to the southern arid zone [6].

According to the calculated dependences, the intensity of chemical weathering at a temperature increase by 0.5 and 1°C should not result in any insignificant increase in the total dissolve salts (TDS) of waters in northern areas. However, a notable increase (by about 25%) in the total concentrations of salt should occur in central and southern regions of the European part of Russia at a temperature increase by 2°C. A significant increase (by approximately 50%) in the total phosphorus concentration in lake waters should occur practically everywhere (except only tundra and forested tundra territories) already at an increase in the average daily temperatures by 0.5°C. Phosphorus concentrations should particularly increase in arid zones, in which climate warming should result in significant eutrophication of the waters.

Lately acquired data indicate that temperature in the Arctic has significantly increased, and this resulted in a notable increase in concentrations of nutrients in the waters [9], which will be discussed below. Climate warming thus changes not only hydrological conditions under which the waters are formed but also modifies the chemical composition of the waters: the salt concentrations increase, as also do the concentrations of nutrients, and this should be most clearly seen in southern regions and also be discernible in the Arctic (Figure 3).

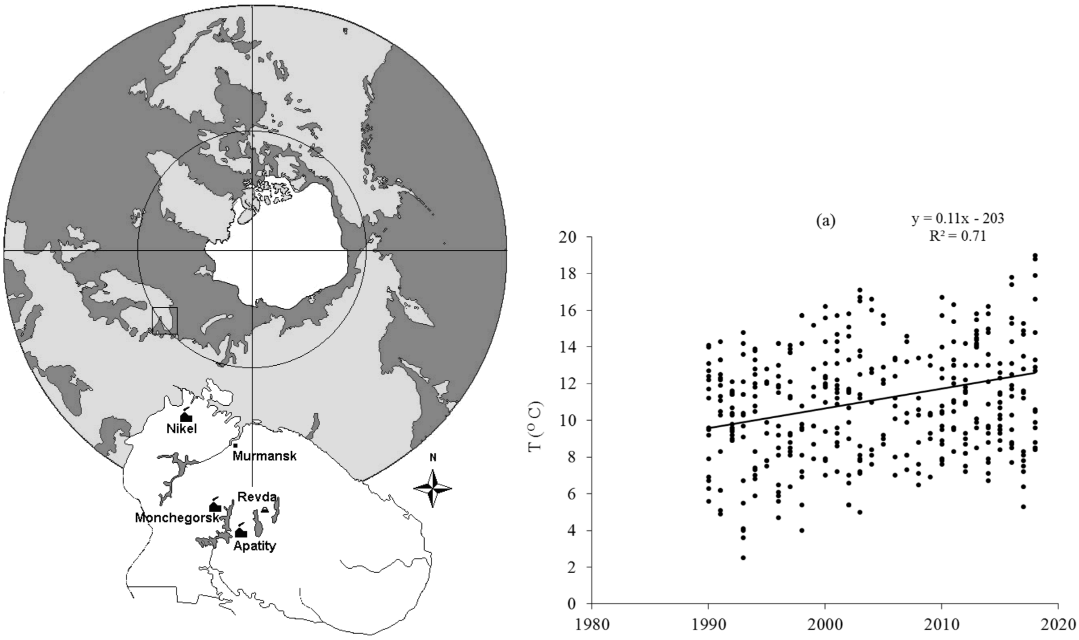


Figure 3. An example of an increase in mean monthly surface air temperature T (C) a 28-year period (1990-2018) on the territory of the Kola North. Significant positive slope of the temperature (T) SKT = +4.71, $p<0.001$. Quoted from [9].

4. Eutrophication

Climate warming most significantly affects the biogeochemical cycling of nutrients and organic matter by stimulating eutrophication. Eutrophication is greatly contributed by global anthropogenic dispersion of phosphorus and nitrogen. The main reason for the rocketing eutrophication of the freshwaters is the increase in nitrogen and phosphorus anthropogenic loads on the environment, a process that has manyfold intensified worldwide over the past years [12, 32-34].

The overall runoff of phosphorus to the ocean is evaluated to has nine- to tenfold increased compared to the preindustrial period. Natural phosphorus comes to the environment at the chemical weathering of rocks, and approximately 1.1 million tons of natural phosphorus is annually introduced into the natural cycling of this element. Several models suggest that global phosphorus loads in the runoff and leaching into freshwater may vary from 0.16 to 5 TgP per year [35, 36].

Anthropogenic activities modify the cycle of another nutrient element: nitrogen, with N2 converted into reactive nitrogen is a consequence of the following four processes: industrial chemical binging (80 MegatonsN per year); agricultural chemical binging through the cultivation of leguminous (40 MegatonsN per year); combustion of effluent gases (20 MegatonsN per year); and biomass combustion at fires (10 MegatonsN per year) [37]. Both phosphorus and nitrogen are produced mostly for increasing agricultural productivity. Nowadays it is not possible to limit fertilizer treatments of soils because it is necessary to increase agricultural productivity for providing food for the ever-growing planet's population. NOx emissions prevail in countries with a high GNP, whereas NH3 is emitted mostly in countries oriented on food production [38].

Eutrophication is hazardous for waters utilized for drinking-water supply, fish farming, recreational purposes, and industrial needs because this process intensifies the growth of cyanobacteria and aquatic macrophytes and thus decreases the oxygen contents and leads to the death of the aquatic flora and fauna. The state of thousands of lakes,

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mouths of reservoirs, and wetlands near large population centers worldwide worsens because of the increase in the nitrogen and phosphorus concentrations [39,40].

The eutrophication of waters in the Arctic basin is still inadequately poorly described in the literature. No such problem in mentioned in AMAP reports [18,41]. At many conferences related to studies of the Arctic basin, eutrophication of water bodies at high latitudes is not discussed at all even in the context of climate warming. Eutrophication is undoubtedly hampered by such natural features in the areas as a significant contribution of atmospheric precipitation, the intense flowage of the lakes, and low temperatures. Most lakes in the Arctic zone are oligotrophic (their surface areas are >20 km^2) and dystrophic (bogged lakes highly enriched in humic acids, their surface areas are usually <20 km^2). The large lakes (>100 km^2) are usually thought to be oligotrophic because the effect of allochthonous organic matter on the chemical composition of the natural waters is not as significant.

Northern regions of our planet abound in small oligotrophic lakes that are not directly affected by any aspects of human activities. Cambell et al. [26] have demonstrated the effects of temperature on the biogeochemical cycles of nutrients in some other lakes. With regard to the classification of lakes in the Kola Peninsula based on their phosphorus concentrations, the number of lakes with low phosphorus concentrations has decreased over the past three decades, whereas the number of lakes more corresponding to the meso- and eutrophic types in terms of phosphorus concentration has simultaneously increased [9]. According to [42], practically no oligotrophic lakes is left nowadays in America even in the situation of lakes not impacted by anthropogenic activities.

In the long period of the polar winter, an oxygen deficiency develops near the bottom because accumulated organic matter are oxidized. In spite of the low, anoxia develops by the end of the wintertime in the bottom water layers. This phenomenon can lead to the death of the northern benthic fauna, which is demanding on oxygen. In areas where basins in the Arctic are affected by eutrophication, the role of green, cryptophyte, and cyanobacteriae in the total phytoplankton biomass increases [10].

5. Acidifying compounds

Human activities in the 20th century, first and foremost, the combustion of fuel-oil residue and fossil oil, as well as smelting operations, resulted in vast atmospheric emissions of acidifying gases (SO_2, NO_x, NH_3), which can be converted into acids in the atmosphere and ecosystems and thus lead to the anthropogenic acidification of the waters. The emission levels of anthropogenic sulfur in Europe and North America began rapidly grow starting in the early 20th century and reached a maximum in the mid-century [43]. Water acidification had been discernible in acid-sensitive regions in many countries worldwide by the 1960s and continued to intensify in the 1970s through 1990s. Numerous lakes with low pH of their water and devoid of any living organisms were identified in Scandinavia and eastern United States. Because of the hazardous character of this phenomenon, the International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP-Water) was established in the 1980s to join efforts of all researchers studying the acidification of waters [44].

A number of international decisions and resolutions issued in the 1980s were aimed at reducing the emissions of acidifying gases and eventually led to a reduction of acid loads onto catchments in central Europe and North America. Surface waters in many acid-vulnerable regions began partly recover from their acidification in response to the reduction in SO_2 and NO_3 emissions [45-50]. In spite of the significant reduction of SO_2 emissions over the past fifty years in North America and Europe, as well as in China starting in 2005 [51], acidic precipitations at catchments still exceed their level during the preindustrial period and are going to increase (Table 1).

Table 1. Predictive scenario of anthropogenic emission of acid-forming substances from natural and anthropogenic sources, converted to equivalents of produced acids [52].

Acid equivalent	1990	2000	2025	2050	2100
		Natural			
SO_x, million t-eq	1,0	1,0	1,0	1,0	1,0
NO_x, million t-eq	0,4	0,4	0,4	0,4	0,4
		Anthropogenic			
SO_x, million t-eq	1,8	1,9	2,9	3,8	3,6
NO_x, million t-eq	1,4	1,5	2,3	3,0	4,1
TOTAL	4,6	4,8	6,6	8,2	9,1

While countries in America and Europe had principally reduced the emissions in the 1970s through 1980s, but the emissions continued to increase in the Russian Federation and China, and it was not until 1995 that a tendency started to be discernible toward a decrease in the emission of acidifying gases, first of all, sulfur dioxide [53-55]. Duan et al [56] have demonstrated that, in spite of decades of significant loads of acidic fallouts in Eastern Asia, the problem of water acidification is not as severe because the geochemical structures of the catchments are well capable to neutralize acidic fallouts. These data are consistent with the calculated critical loads at catchments in China [57].

Acidic precipitation modify the transport fluxes of chemical elements in the Earth's shells, intensify the chemical weathering and leaching of major cations and anions, change the biogeochemical cycles of elements in the atmosphere, and freshwater hydrosphere, and kill living species susceptible to low pH. The intensity of water acidification is controlled by the following two major factors: (i) the level of airborne anthropogenic load of acidifying compounds on the catchments, with regard to the exposure time, and (ii) the natural susceptibility and vulnerability of the territories to geological, landscape–geographical, and climatic conditions. If the structure of a catchment and its soils are acidic, the waters should be acidified fairly quickly, because protons (H^+) and aluminum ions (Al^{3+}) should accompany mobile anions (SO_4^{2-} and NO_3^-) and the water currents formed at the catchments. It the buffer capacity is higher, then the progress of acidification should depend on the volumes of acidifying agents accumulated at the catchments [44,46,47,51]. In the European part of Russia and in West Siberia, acidified lakes were found [8] even in areas devoid of acid loads.

The global and regional reduction in the emissions has led to the recovery of acidified waters on all continents. Analysis of literature data led us to distinguish the following three scenarios for the development of long-term changes in the chemistry of waters at a reduction in acidic fallouts [7,42,45,46,47,49]: (i) the acidification of the waters continues, (ii) neither the pH nor the alkalinity of the waters changes, and (iii) the acid-neutralization capacity (ANC) of the waters is recovered. The uneven character of the recovery tendencies in various countries and regions at similar reductions in the contents of sulfates in the waters is explained by features and circumstances at which the waters are formed at the catchments. The influx of basic cations (BC) from the catchment plays a leading role in forming differences at the recovery of the buffer capacity of the waters.

Similar tendencies were identified in the evolution of some other parameters of water chemistry at a reduction in acidic fallouts: an increase in the content of dissolved organic carbon (DOC), nitrogen, and phosphorus. Using long-term data on the increase in carbon concentrations, Corman et al. [58] have determined that an increase in DOC content in a water body is associated with a significant increase in the contents of nitrogen and phosphorus in the lake, and this process is associated with a simultaneous increase in TOC. This phenomenon was named brownfication and was identified in waters in some areas in North America and Europe [45,59,60]. A number of hypotheses were put forth to explain the increase in the content of organic matter in the aquatic systems. Montaith et al. [45] believe that this process is related to the role of humic acids at the recovery of the

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chemical composition of lake waters after their acidification over the past two to three decades. Lately many researchers explained this phenomenon by the additional effect of climate warming [9,27,48,61].

6. Contamination of the Waters with Toxic Compounds

Toxic contamination of waters is one of the most hazardous processes. Toxic properties of chemical elements and compounds are understood as their ability to adversely effect on living organisms. It is widely known that many newly synthesized compounds are highly toxic to living organisms. It is also known that industrial byproducts and many naturally occurring elements in atypically high concentrations, for example, the essential metals, such as Cu and Zn, are also toxic to living organisms [62-65]. Aquatic systems are collectors of all toxic elements and compounds known to occur in the environment, and the implications and consequences of this phenomenon are still not fully understood because they may manifest their hazardous properties even if occurring in low concentrations. Coming into aquatic systems, toxic elements and compounds may circulate and be accumulated when moving along the food chains.

All ecologically toxic compounds can be grouped into the following classes:

1. Metals and metalloids, which are elements occurring in nature and toxically affecting living organisms when in high concentrations or in certain speciation;
2. Persistent Organic Pollutants (POP_s), which are industrially synthesized compounds or byproducts of some technological processes involving naturally occurring compounds. This group comprises a broad class of organic xenobiotics: herbicides, insecticides, dioxins, furans, phthalates, etc.

Some contaminants are brought to the environment because of technological disasters, such as oil spills, massive discharges (and/or leaks) of toxic compounds, and protection-dam breaks at tailing dumps. Natural disastrous events, such as volcanic activity and fires, can also release toxic compounds in concentrations harmful for living organisms. One of the examples in mercury [66].

Metals and metalloids. Metals are brought to water arteries with the runoff from various industrial facilities, diffuse sources, and are leached from rocks by acidic precipitation. The dispersion of chemical elements is facilitated by mining operations and smelting. Anthropogenic activities result in that the volume of metals coming to water bodies due to anthropogenic processes are comparable to the naturally occurring fluxes of these metals (Table 2). The number of publications on the levels of metal concentrations in water, sediments, and biota, as well as their toxic properties (experimental data), is high and continues to increase [67,68].

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Table 2. Natural runoff of metals with rivers and anthropogenic input of elements into the environment and lakes, including metals (according to estimates by various authors: 1) –Bryan [69]; 2) –Moore, Ramamurth [70]; 3) –Venitsianov, Lepikhin [71]; 4) –Heath [72].

Metals	River runoff by chemical weathering	Inflow to lakes (according to our calculations)	Dispersion Into the environment
Cr	60,0 3)	63	54-130 3)
Mn	440 1)	2903	-
Fe	25000 1)	31925	-
Ni	300 1)	161	47,4 2); 43-98 3)
Cu	375 1)	229	56 2); 56-263 3)
Zn	370 1)	693	314 2); 315-840 3)
Mo	13 1)	92	-
Ag	5 1)	3,9	-
Cd	4,65 3)	43	7-11 3)
Sn	1,5 1)	26	-
Sb	1,3 1)	22,2	-
Pb	180 1);	119	449 2); 360-440 3)
Hg	3 4)	-	5 – 10 3)

Two regions north of the Arctic Circle, the Kola Peninsula and Norilsk area, are the most ecologically alarming in terms of water contamination with heavy metals (2020). It has been proved that a broad spectrum of metals (Ni, Cu, Mn, Sr, Fe, Al, Co, Cr, Cd, and Pb) migrates in Arctic water bodies dominantly in the form of ions, which are the most toxic. The toxic properties of the metals are enhanced at the associated eutrophication and acidification of the waters. The acidic atmospheric precipitation intensifies the leaching of metals from rocks, and this even further enhances the hazardousness of the metals in acidic waters [73].

At accompanying eutrophication and the development of oxygen deficit in Arctic regions, the desorption of metals from bottom sediments is responsible high gradients of the dozes of their toxic effects in the bottom water layers for the fauna during long wintertime in the Arctic. The mechanism of the redox cycle has been thoroughly studied for Mn and Fe. These elements ascend in the form of dissolved reduced species to the oxicline boundary, into oxygen-enriched water layers, where these metals are oxidized again, form low-solubility compounds, and precipitate to the bottom, where the aforementioned cycle is restarted under reduced conditions. Data on the layer by layer distribution of elements in the water column of an Arctic lake indicate that a concentration gradient is thus produced not only for Fe and Mn but also for a large group of other elements, such as Cd, Hg, Cu, Mo, Ni, Pb, Zn, Cr, Co, Ba, Ga, and U. A generalized scheme of the metal cycle in the Arctic waters is presented in the work [4].

The world's scientific community currently pays much attention to such hazardous elements as Hg, Cd, and Pb. In water bodies in the studied areas of the Arctic, Hg concentrations were very low, whereas the accumulation of this elements in various organs and tissues of the fish indicates that the regional waters are ubiquitously contaminated with Hg. The lakes contain Pb mostly (>70%) in the form of its ionic species, which are able to readily penetrate into the fish organism. This element is accumulated in all systems of the fish organism depending on Pb concentration in the water. Cd is accumulated in all systems of the fish organism, and its highest concentrations were found in the kidneys [74].

Nowadays, environment-protection administrating bodies declare that methods for the evaluation of the biological availability of elements should be incorporated into procedures for the assessment of risks of water pollution with metals and into ecological management of water quality [10,75-77]. For example, the Water Framework Directive assumed in the European Community stresses that standards for water quality should include bioavailable Ni and Pb species [78]. The United States Environmental Protection Agency (EPA) has introduced a tool for assessing the bioavailability of Cu in standards for water contamination with this metal [79]. The models rely on the determination of the amounts of metal ions of the greatest penetrating capacity, i.e., bioavailability. While the standards assumed for Hg in Russia are comparable to those in the West, those for Pb and Cd are much more strict in Europe and the United States.

Persistent organic pollutants (POPs). These are industrially produced compounds that can be retained for years in the environment and be accumulated in fatty tissues. POPs include pesticides, such as aldrin, chlordan, DDT, dieldrin, endrin, heptachlor, hexachlorbenzene, mirex, α- and β-hexachlorocyclohexane, chlordecone, and lindane, as well as industrially manufactured chemical compounds, such as polychlorobiphenyls, hexachlorobenzene (which is also a pesticide), hexabromdiphenyl, hexa- and- heptabromdiphenyl ether (commercial octabromdiphenyl ether) , pentachlorbenzene, perfluoroctane sulphacid and its salts, perfluoroctane sulfonyl fluoride, tetra- and pentabromdiphenyl ether (commercial pentabromdiphenyl ether), and such unintentional byproducts as polychlorinated dioxins and furans [80]. These highly toxic compounds can come to the environment as a result of various anthropogenic activities, can be transported for long distances with air and waters, and are able to make up hazardous concentrations in waters [68,81,82]. In 2021, the European Commission adopted a proposal to protect human health and the environment from some of the most harmful chemicals in waste: POPs. The convention provided for the possibility of appending the current list of compounds by other ones with the accumulation of necessary information, if the newly introduced compounds have principal characteristics of POPs: high stability in the environment, resistance to degradation, acute and chronic toxicity, bioaccumulation, and the ability to be transferred across boundaries for great distances in the environment [81,82]. Table 3 lists time periods needed for the decomposition of these compounds. These data show how long these compounds can be retained at a catchment and/or in a water body.

Table 3. Half-life of some xenobiotics in the environment [83].

Pollutant	Half-life in temperate climates			
	Air	Water	Bottom sediments	Soil
DDT	2 days	> 1 year		
TCDD	9 days	> 5 years	> 1 year	10 years
Aldrin	< 9 hours	< 590 days	no data	5 years
Dieldrin	< 40,5 hours	> 2 years	no data	> 2 years
Endrin	1,45 hours	> 112 days	no data	< 12 years
Chlordane	< 52 hours	> 4 years	no data	1 year
Heptachlor	no data	< 1 day	no data	120 – 240 days
Hexachlorobenzene	< 4,3 years	> 100 years	no data	> 3 years
Mirex	no data	> 10 hours	> 600 years	> 600 years
Toxaphene	< 5 days	20 years	no data	10 years
PCB	3 – 21 days	> 5 days	no data	> 40 days

The behavior of these compounds in aquatic ecosystems is characterized by that the compounds can be strongly accumulated in aquatic systems because of gradual enrichment in the food chains.

The adverse effects of toxic compounds at their direct of diffuse introduction into lakes and rivers commonly manifest themselves through the chronic effects of low concentrations. In these situations, either disturbances are slowly (and often imperceptibly) accumulated in the aquatic organisms and may manifest themselves with the passage of time or in some critical situations, for example, when the temperature is anomalously high, during rain flooding, at stormy weather, etc. [63]. Chronic effects are more difficult

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to identify in spatiotemporal sections, and their identification requires long-term observations of the organisms, populations (during a few iterations), and communities. In spite of great progress in studying consequence of toxic contaminations, it is still not possible to predict all remote aftermaths of small dozes of chronic contamination [5,64,84-86].

7. Critical loads: theoretical approaches

Along with other safety types, the ecological one is now one of the principal challenges on this planet because of the complexity, multiaspect nature, and the importance and extent of the emerging ecological problems. It is hard to suggest either an adequate monitoring program or rational measures aimed at data acquisition and processing without preliminary reasonably profound studying of how the quality of waters and their characteristics are formed, which are the mechanisms of response of organisms and ecosystems to various anthropogenic impacts. Evidently, the principle of precluding contamination of aquatic systems instead of fighting consequences of this contamination should be viewed as one of the guiding lines.

A large team of scientists [11] have analyzed the historical epochs of critical states to identify permissible (threshold) loads for principal anthropogenic loads, i.e., to determine the ability of ecosystems and the biosphere as a whole to deal with anthropogenic fluxes of chemical elements and compounds without causing harm for living organisms. Many scientists believe that now threshold concentrations are exceeded for the increase in the CO_2 content, fluxes of phosphorus, and some other factors. It is however hard to say how much can be warranted is to apply global constraints to individual aquatic systems. Many water bodies on our planet are significantly contaminated with various wastes, whereas vast other areas are not affected by anthropogenic activities at all, such as large territories in West Siberia and the Russian Far East and several areas in Africa and South America.

Over the past decades, the concept of critical loads was developed as a scientifically justified strategy for precluding the degradation of natural complexes and control of the state of natural objects. Thereby critical loads are understood as the maximal permissible influxes of one or more contaminants into an ecosystem that do not induce adverse changes in the most vulnerable links of the system (as estimated at the current state of knowledge). When determining the certain permissible (critical) loads in real natural systems, it is necessary to solve complicated fundamental problems of the science of Earth and life, such as:

1) behavior patterns of anthropogenically introduced elements, interaction with natural factors, involvement in the natural cycles of elements, and the bioavailability of ecotoxicants and
2) stability mechanisms and variability limits of biological systems, the long-term consequences of anthropogenic contaminations for living organisms, and the estimation criteria.

Until these problems are solved, it is not possible to determine how long a natural environment is able to assimilate the influx of contaminants without adverse consequences for the preservation of survival conditions. A flow chart of an algorithm for the calculation of critical load and management of the anthropogenic impacts is presented in Figure 4. This diagram reflects the convergence of various fields of science aimed at studying ecological processes and real aquatic systems. As demonstrated above, nowadays multiple and diverse anthropogenically induced phenomena and processes occur in nature, in which organisms and ecosystems are affected by resultants of all direct and indirect effects of numerous contaminants, climatic factors, and changes in landscapes and biogeochemical cycles.

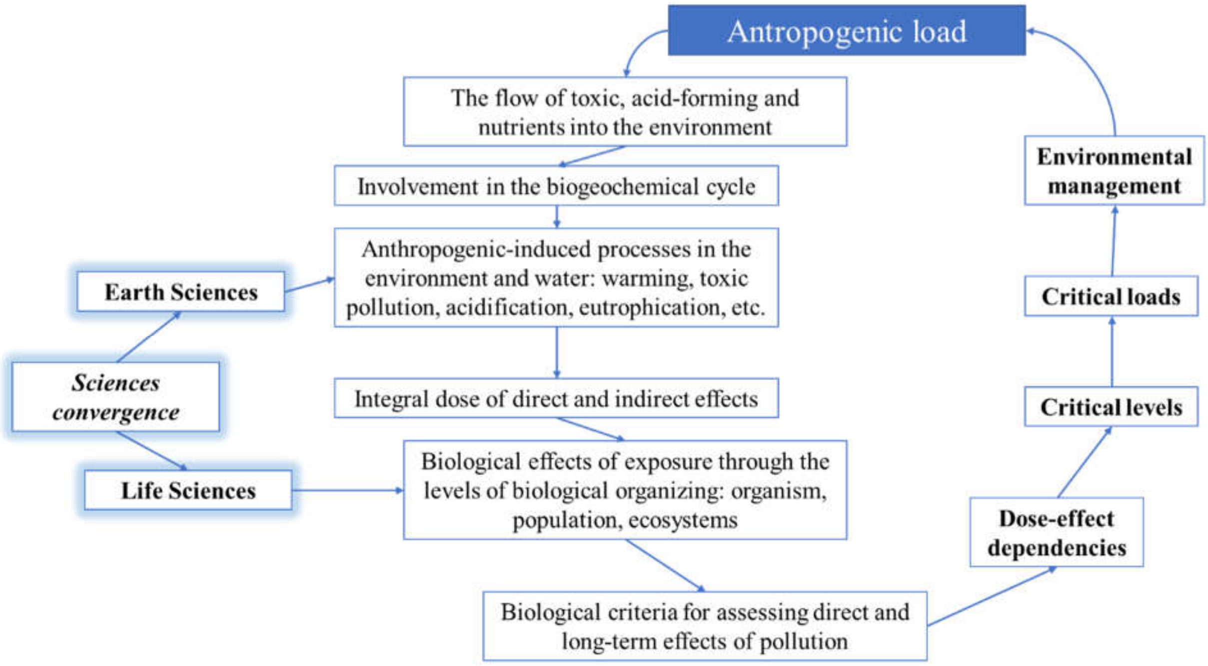

Figure 4. Flowchart of the estimation of critical loads and management of anthropogenic impacts.

The international practice offers examples of calculations, which were conducted using methods devised for the evaluation of critical loads, of the necessary levels to which the transfer of some hazardous compounds into terrestrial and aquatic ecosystems should be reduced. The acquired scientifically justified data provided a basis for making international decisions on the reduction of emissions of the most hazardous contaminants (such as the Gothenburg Protocol on the reduction of emissions of acidifying gases, the Stockholm Convention on Persistent Organic Pollutants, the Minamata Convention on Mercury, etc.). Modern science makes provide means for calculating the permissible fluxes of nutrients into aquatic systems, and the application of these estimates resulted in the oligotrophication of some lakes and rivers, in the recovery of water quality after acidification in some water bodies in Scandinavia and North America. The decisions were made based on fundamental studies aimed on determining critical loads.

8. Conclusions

The anthropogenic load on surface waters increases in spite of the significant reduction in atmospheric emissions and discharges of industrial wastewaters and agricultural sewage in the current century. Climate warming in combination with the dispersion of nutrients ubiquitously results in the eutrophication of waters as a global process. The contents of organic matter and nutrients in surface waters increase, and this decreases the number of oligotrophic lakes and leads to the deterioration of water quality at cold latitudes as a consequence of the eutrophication of water bodies at climate warming.

The amounts of anthropogenic produced sulfates decrease as a consequence of the reduction of SO_2 emissions, which enhances the acid-neutralizing capacity of the waters of vulnerable lakes (in terms of the geological structure of their catchments). However, biogeochemical cycles do not return to their original natural parameters, and simultaneously the contents of organic matter and nutrients increase, which modifies the cycling of compounds in the catchment–water body systems.

The migration activity of metals is enhanced, they come to be involved in transport flows, usually in the form of organometallic complexes. The most biologically available and ecologically toxic species of metals are their ionic compounds, except only highly lipophile metals (Hg). The contents of organic xenobiotics in surface waters decrease as a consequence of constraints placed on their use in well-developed countries. Organic ecotoxicants involved in biogeochemical cycles continue to migrate in terrestrial waters as a consequence of the global dispersion of these compounds in the past.

Many lakes and rives are recovering, and the quality of their water has improved. For example, oligotrophication was detected in some large lakes worldwide, the number of acidified small lakes decreases, and the fluxes of toxic compounds into rivers and lakes are reduced. At the same time, the aquatic systems do not return to their original natural parameters, and the ecosystems and biogeochemical cycles reach new states, which are different from the natural ones. The comprehensive and profound understanding of interrelated transformations of the inert and living matter under the effect of human activities provides a basis of the evaluation of permissible constraints aimed at maintaining ecological safety.

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