

Biological oxygen demand in soils and hydrogel compositions for plant protection of the rhizosphere

Andrey Valentinovich Smagin

Institute of Forestry, Russian Academy of Sciences, ul. Sovetskaya 21, Uspenskoe, Moscow oblast, 143030 Russia; Moscow State University, Leninskie gory 1, Moscow, 119991 Russia.

smagin@list.ru

Abstract. Potential biological activity of mineral and organogenic samples from light-textured sod-podzolic soils as well as of hydrogel compositions for protecting the root layer from pathogenic microflora and unfavorable edaphic factors were studied in laboratory conditions by oxygen consumption under the optimal hydrothermic conditions with portable gas analyzers. We have conducted ecological standardization of biological activity and organic matter destruction estimated by biological oxygen demand (BOD) in the widespread sandy soils. The primary outcome was the scale of gradations of biological oxygen uptake in soils with a range of quantities of potential biological activity from "very low" ($<2 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$) to "extremely high" ($>140 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$), obtained on the basis of statistical processing of data array 1308 measurements. Acrylic polymer hydrogels had $\text{BOD} = 0.2\text{--}2 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$, which corresponded to the periods of their half-lives from 0.2 ± 0.1 to 6.8 ± 4.5 years, or relatively low resistance to biodestruction. In contrast to the pure gels, hydrogel compositions for rhizosphere based on ionic and colloidal silver showed low biological activity ($\text{BOD} = 0.01\text{--}0.2 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$) and, accordingly, significant resistance to biodegradation with half-lives from 5 to 70 years and above.

1. Introduction

Biological or biochemical oxygen demand (BOD) is commonly used to evaluate the biological activity in the environment. It has become the most widespread in biochemistry of environmental water and toxicology, as a way to assess the capacity of microbial organisms to decompose organic matter, organic wastes, including pollutants in the aquatic habitat and sediments [1–4]. Experimental assessment of BOD in soils is an uncommon practice, as the biological activity of soils is usually evaluated by another component of respiration – emission of carbon dioxide [5]. Solvita, the test for soil respiration and the system of biological activity grading based on CO_2 emission, which has been developed mostly for agricultural soils, is heavily used in actual practice [5, 6]. Current grading system is inapplicable to forest or peat soils, as CO_2 emission from the organic horizons (peat, forest litter) can be 1–2 orders higher than the upper limit of 12 mg/kg/hour proposed by [6]. Due to the same reason it is virtually impossible to use this system for the analysis of biological degradation in artificial soil constructions, which include organic soil modifiers (peat, mixed composts, humates) or synthetic hydrogels with high biological activity [2, 7, 8]. Moreover, the assessment of biological activity and biodegrading properties of soils by CO_2 emission has a number of serious methodical complications that are primarily related to interphase interactions of the gas in soil medium [8, 9]. Implication of BOD, on the contrary, allows one to avoid these problems, as oxygen, unlike CO_2 , is poorly soluble in



water and is much less adsorbable. It also enters the soil from a virtually unlimited air reservoir with constantly high concentrations of oxygen, which maintains equilibrium state of oxygen throughout all the physical phases of soil (solid, liquid and gaseous). Modern technological advances related to quantitative analysis of oxygen content provide a solution to the issue of BOD assessment instrumentation [8, 10-12]. Current paper contains the results of BOD assessment by portable electrochemical gas analyzers in widespread sandy soils of the Moscow Region, related to their performance by soil conditioners of the new generation in the form of strongly swelling polymer hydrogels (SSPH) and their composites with ionic and colloidal silver as a means of protecting the root systems of natural and cultural plants.

2. Materials and methods

Soil samples were selected at suburban forest, forest park and fallow objects, belonging to the Institute of Forest Science of the RAS and continually exposed to intense anthropogenic impact, caused by Moscow megalopolis. The soil cover under natural coniferous and mixed coniferous-deciduous forests was represented by sandy and loamy-sandy soddy podzolic soils with organogenic (forest litter) and mineral (humus, eluvial, and illuvial horizons, parent material) layers. During the period of research from 2002 to 2016 yrs, we selected 436 soil samples, including 95 organogenic horizons, what in triplicates gave 1308 measurement of BOD.

The main method of study was the incubation of samples in closed flasks with subsequent assessment of soil respiration through the rate of oxygen consumption [8, 9]. A closed flask with soil provides proper conditions for development of the microbial population and degradation of organic substrates. For this purpose, precalculated amount of water is added to the air-dried soil samples to obtain the optimum moisture – 0.7-0.8 units of the soil-saturation moisture. Moist samples in tight-sealed flasks were placed in a thermostat with the optimum temperature of incubation of 25-30°C. Eventually, after a certain amount of time Δt (usually around one day), the decrease in the oxygen volume proportion (ΔX) of the gas in the flask was measured and BOD (uptake per unit mass, U_m) was calculated per unit soil solid phase mass (m_s), as follows [8, 9]:

$$U_m = (\Delta X \cdot P \cdot M \cdot V_g) / (100 \cdot R \cdot T \cdot \Delta t \cdot m_s), \quad (1)$$

where R is the universal gas constant ($8.314 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$), T – absolute temperature (K), P – atmospheric pressure (Pa), M – molar weight of the gas ($\text{g} \cdot \text{mole}^{-1}$), V_g – volume of the gas phase in the flask (ml). On substituting the formula parameters in the listed units and the variables – gas volume proportion (ΔX) – as percentage, time (Δt) – in hours and weight of absolute dry soil or any other incubated material (m_s) – in grams, we get the result in milligrams of gas per kilogram of soil per hour ($\text{mg} \cdot \text{kg}^{-1} \cdot \text{hour}^{-1}$). The volume proportion of O_2 in the air samples from the flask was determined, using portable gas analyzers MGL-18 and PKG-4 (Russia) with electrochemical oxygen detectors.

The hydrogel compositions were prepared on the basis of 5 types of strongly swelling polymers: №1 – acryl hydrophilic Aquasorb preparation (Germany) with high degree of swelling (HDS) in pure water (700–1000 g $\text{H}_2\text{O}/\text{g}$); №2 – radiation-cross-linked technical polyacrylamide, synthesized in Institute of Chemical Physics of the Russian Academy of Science [7, 8], with HDS in pure water 700–1000 g/g, and in saline solutions of 0.01–0.1n concentration at least 250–500 g/g; an experimental batch of acrylic gels with HDS in pure water 500–700 g/g from the Ural Chemical Company, prepared using proprietary technology [13] that included samples №3 – with hydrophilic filler in the form of waste biocatalytic production of polyacrylamide, №4 – with amphiphilic excipient in the form of humates, and the addition of microelements, №5 – with amphiphilic excipient in the form of dispersed peat. Silver, as an inhibitor of biological activity, and as a component of protective gel compositions in the colloidal form (experienced products of CG Agro-Chemical Industry (Russia) with amphiphilic surfactant-stabilizers) and in the form of ionic (AgNO_3) solution were added to SSPH in the concentration (for the active substance – Ag) 10, 100, 1000 ppm per mass of water in swollen hydrogel. Samples of hydrogels and their composites with silver were incubated as described above. Variants of the experiments included pure gel compositions, and their mixtures with water extracts of rotting potato tubers and calcined to 500 °C sandy soil substrates. Hydrothermal conditions of the experiments

were chosen according the degree of swelling of SSPH 100 g/g in pure gel compositions that in soil-gel mixes gives 1:1 ratio of water and mineral components. The temperature of incubation was carried out in the range of 20-35 °C with subsequent recalculation on the optimum temperature for microorganisms (30 °C), according to [8, 9]. Calculation of effective half-life ($T_{0.5}$) from the data of the BOD (U_m) and percentage carbon content (C%) of SSPH was carried out according to the exponential model of organic matter biodegradation for aerobic oxidation (1 mol CO₂=1 mol O₂) in the form of the following ratio [8]:

$$T_{0.5}/T_0 = \ln 2 / (\ln 1 - \ln(1 - 10^{-4} \cdot T_B \cdot 12 \cdot U_m / (32 \cdot C\%))), \quad (2)$$

where $T_0=1\text{yr}$ – is the time scale for the process of biodegradation, $12/32$ – the ratio of the molar masses of carbon and oxygen, T_B is the average yearly period of biological activity, expressed in hours.

3. Results of study

Figure 1 shows general probability distribution of BOD values over the classes, regarding all the studied soil objects. It is bimodal, which is related to qualitative differences between two main varieties of the studied samples – organogenic (forest litter) and mineral (humus, elluvial, illuvial horizons). Relatively high BOD values (100-800 mg·kg⁻¹·hour⁻¹) at low soil bulk densities (up to 0.5 g·cm³), present in forest litter, and, conversely, relatively low BOD values (less than 40 mg·kg⁻¹·hour⁻¹) at densities of 1 and higher, inherent to mineral horizons. Modal classes of biological activity (10-20 mg·kg⁻¹·hour⁻¹ for the mineral soil materials and 300-400 mg·kg⁻¹·hour⁻¹ for the organogenic ones) differ more than by an order of magnitude. We tried to smooth such strong differences by entering the index of volumetric BOD by multiplying U_m and soil bulk density (ρ_b):

$$U_v = U_m \cdot \rho_b \quad (3)$$

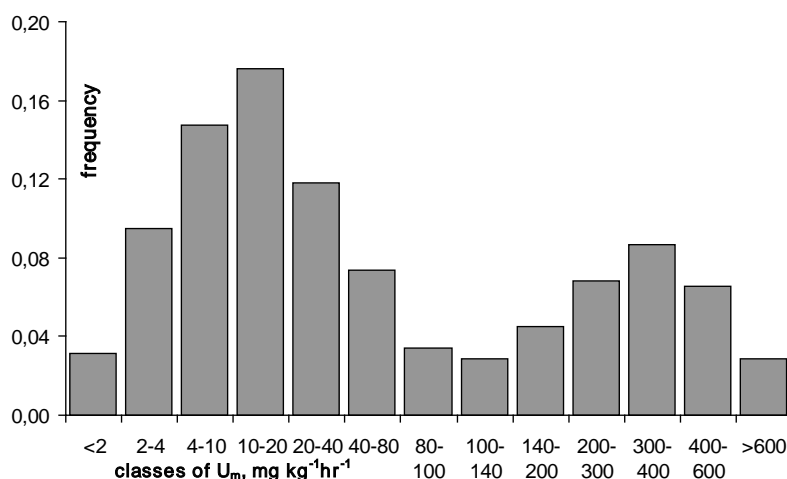


Figure 1. The frequency distribution of the specific BOD (U_m) in coarse-textured sod-podzolic soils with litter.

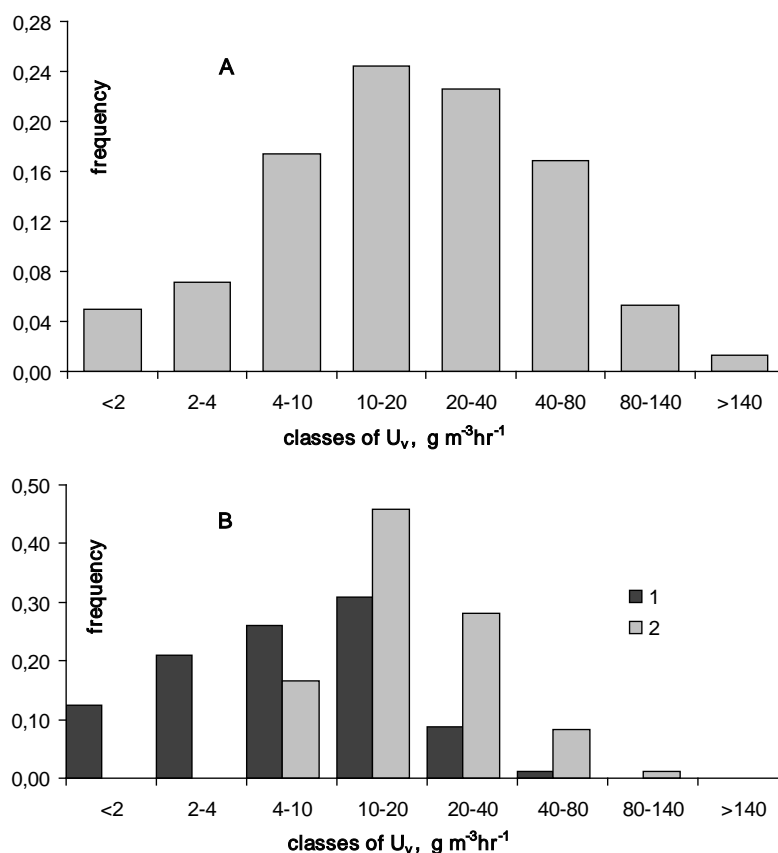


Figure 2. The frequency distribution of the volumetric BOD (U_v) coarse-textured sod-podzolic soils: **A** – general distribution, **B** – mineral horizons; 1 – under anthropogenic load, 2 – without load.

As $1\ g/cm^3 = 1000\ kg/m^3$, the product of U_m in terms of $mg\cdot kg^{-1}\cdot hour^{-1}$ by soil density in terms of g/cm^3 will be numerically equal to the volume uptake in terms of $g\cdot m^{-3}\cdot hour^{-1}$. The physical significance of this value is the rate of oxygen consumption by a volume unit of soil. This parameter does not depend on soil bulk density that much, allowing one to compare soils and soil materials of different nature. Indeed, general probability distribution of the new parameter, unlike the initial one, is unimodal with at least four times narrower range of values (Figure 2). In case of respiration scaled to mass, the range was $0-600\ mg\cdot kg^{-1}\cdot hour^{-1}$, while the data spread of the volume parameter was virtually within the range of $0-140\ g\cdot m^{-3}\cdot hour^{-1}$ with the most probable values (modes) of $10-20\ g\cdot m^{-3}\cdot hour^{-1}$. The modal classes contained both the data on the organogenic strata and the mineral horizons with the appropriate biological activity.

The new distribution was used as the basis for the grading system of the biological oxygen uptake, shown in Table 1. Let us compare it with the well-known classification [6] on the assessment of standardized soil respiration under optimal conditions by CO_2 emissions. For this purpose we recalculated the respiratory gradations in [6], expressed in $lbs\ CO_2\cdot C\cdot a^{-2}\cdot day^{-1}$ per unit $g\cdot m^{-3}\cdot h^{-1}$, using known conversion: $1\ acre = 0.405\ m$, $1\ lb = 0.454\ kg$, $mCO_2 = 44/12\ m\ C\cdot CO_2$, $1\ day = 24\ hrs$ and data on the average CO_2 emissions depth of $7.6\ cm$ from the [6]. As a result of initial graduation ($<2\ g\cdot m^{-3}\cdot h^{-1}$ – «very low» and $2-4\ g\cdot m^{-3}\cdot h^{-1}$ – «low» biological activity) from the work [6] completely matched our. Subsequently there were some differences in the names and in numerical expression of

Table 1. Grading system for the potential biological activity (by BOD) in sod-podzolic soils of the Moscow Region.

U_v , $g \cdot m^{-3} \cdot hour^{-1}$	Rates of biological activity:	Comments:
<2	Very low	No or very low content of organic matter and (or) suppression of biological activity by pollutants, electrolytes, consolidation and other factors. Soil is unsuitable for vegetation.
2–4	Low	Insufficient levels of natural fertility and (or) substantial pollution, salting and load on soil. Vegetation is suppressed, rare, mostly, ruderal species
4–10	Satisfactory	Low levels of natural fertility and (or) decrease in fertility due to anthropogenic impact. Vegetation production, biodiversity and sustainability are also below average levels
10–20	Normal	Normal soil activity, providing consistent productivity and typical biodiversity of plants (dominant). No or insignificant pollution, salting and other types of man-induced burden.
20–40	Elevated	Organic matter destruction rates are elevated due to favorable hydrothermal conditions or integration of easily decomposed detritus compounds. No disturbances of normal functioning, soil fertility, plant productivity and biodiversity are above average levels.
40–80	High	Soil contains fresh organic substrates, high content of enzymes and favorable hydrothermal conditions. High levels of real soil fertility, providing growth and development of demanding plants, including nemoral species of ground cover and broad-leaved tree species. Anthropogenic burden is absent.
80–140	Fairly high	Common for moder-mull and mull organogenic substrates, consisting mostly of easily decomposed compounds on the surface of soils, not exposed to anthropogenic burden. Under optimal hydrothermal conditions it may lead to rapid destruction of organic matter and, if lacking proper humus deposits in the mineral horizons, to loss of the ecosystem sustainability. Promotes excessive emission of greenhouse gases into the atmosphere.
>140	Extremely high	Common, mostly, for mull leaf litter and detritus. Under optimal conditions for decompositions, promotes total mineralization of organic matter in the warm season and extremely high emission of greenhouse gases. Unless compensated with high production, it leads to disruption of the ecosystem and local deterioration of the atmosphere.

categories of the soil biological activity. Category 4-7 $g \cdot m^{-3} \cdot h^{-1}$ – «medium activity» by [6] in our case increased to 4-10 $g \cdot m^{-3} \cdot h^{-1}$ – and was called «satisfactory activity». The next category of 7-14 $g \cdot m^{-3} \cdot h^{-1}$ – «ideal activity» by [6] can be associated with our version of «normal activity» with the boundaries of 10-20 $g \cdot m^{-3} \cdot h^{-1}$. Further on [6] should be the final category of > 14 $g \cdot m^{-3} \cdot h^{-1}$ – «unusually high activity», which unites our categories 20-40 $g \cdot m^{-3} \cdot h^{-1}$ – «elevated activity» and > 40 $g \cdot m^{-3} \cdot h^{-1}$ – «high activity» with fractional division into three classes (Table 1). Higher values of biological activity compared to [6] in our scale for all classes, except low, can be explained by the following reasons. Firstly, we examined the BOD, but not the CO₂ emission, which is usually lower due to the strong interfacial interactions of CO₂ in soils [8, 9]. Secondly, the work [6] and prior to it methodical development [5] dealt with the mineral, mainly arable soils used in agriculture. In our case soils belonged to the forest type and included along with mineral substrates, organic horizons in the form of litter which has substantially higher values of biological activity. In general, our development does not contradict the earlier and widely used in practice, the system [6], and organically supplements and develops it.

According to the proposed scale (Table 1), low and very low values of biological activity were mainly observed in the soil sand horizons (E, B), in the subsoil extracted to the surface during the earthwork operations, and at the campfire sites, wide paths and trampled areas with no vegetative cover. Satisfactory, normal and elevated biological activity was inherent to both mineral and

organogenic horizons of studied soils, while the recreational burden led to at least one-step shift in the examined parameter towards lower values. The control (no load) organogenic horizons had elevated and high activity, while moderate (regulated) recreation resulted in normal respiration rates, and unconstrained recreation – in normal and satisfactory values. In case of mineral horizons from the background sites with no man-induced load, normal and elevated biological activity was most frequently observed, with no cases of low or very low values (Figure 2). In 10% of cases, even high and very high respiration rates, common for the humus horizons of nemoral parcels of mixed coniferous-deciduous forest, far from paths and roads. Low and very low values of biological activity constituted a large proportion (over 30% of cases) of the distribution for the recreational areas (Figure 2). These values were mostly observed at the sites of massive, uncontrolled recreational burden, while in cases of moderate, regulated recreation, normal and satisfactory respiration rates were prevalent.

At the second part of the paper, let us turn to the results of the experiment on biodegradation of SSPH under the influence of silver inhibitors of the biological activity (Figure 3). The magnitude of BOD of pure SSPH ranged from 0.2 ± 0.09 to $2.03 \pm 0.03 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$, which has met a very low biological activity to the soil, according to Table 1. However, this activity is enough to cause considerable damage to SSPH organic materials in the soils. Basically, the half-time period of microbial decay of SSPH ranged from 0.2 to 3.2 years and only in the sample №5 with amphiphilic excipient in the form of dispersed peat was 6.8 ± 4.5 years. Low resistance of SSPH to microbial decay in soils is confirmed by direct observations and forecast on the mathematical models of biodegradation [7, 8]. Introduction of silver inhibitors of the biological activity significantly reduces BOD and biodegradation in gel compositions. In the case of silver ions under the action of a dose of 10 ppm BOD decreases at 13-30 times (Figure 3-A). The exception is the gel Aquasorb where the BOD is reduced to not more than three times. Doses of 100-1000 ppm inhibit BOD 20-60 times without significant differences on the effects between them. As the result the calculated values for the effective half-lives increase to 5-35 years in SSPH composites with 10 ppm Ag and up to 24-72 years when the content of silver ions ranges from 100 to 1000 ppm. Colloidal silver has a similar inhibitory effect (at the dose of 10 ppm Ag BOD is equal $0.02\text{-}0.3 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$ and $T_{0.5}$ varies from 8 to 35 years, and at doses of 100 ppm Ag BOD is equal $0.01\text{-}0.05 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$ and $T_{0.5} = 72\text{-}144$ years (Figure 3-B).

The addition of extracts of root rot and mixing of SSPH with a sandy soil substrates significantly enhances biological activity (Figure 4). On the control in mixtures of hydrogels without silver BOD is increased to $11\text{-}13 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$ when adding putrefactive microorganisms (priming effect) and up to $3\text{-}4 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$ in case of their absence. It meets the normal or low biological activity of soils according to Table 1 and a small stability of all investigated SSPH in soils with half-lives $T_{0.5} = 0.2\text{-}1.2$ years. Incorporation of ionic silver is effective only with large doses of 100-1000 ppm, which reduce BOD in 5-10 times to values of $0.2\text{-}0.6 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$ (Figure 4-A). The magnitude of $T_{0.5}$ increases in this case up to 3-7 years. A low dose of silver ions at 10 ppm has a opposite stimulation of biological activity that is probably due to adsorption of Ag^+ by negatively charged surface of soil particles and increased growth of the microflora under the influence of nitrate anions remaining in the solution. Colloidal silver has a more powerful inhibitory effect in mixtures of SSPH with soil substrates compared to the ionic forms (Figure 4-B). Under the influence of a low dose of 10 ppm Ag the index of volumetric BOD is reduced to 6-40 times to values of $0.3\text{-}3 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$. Especially effective action of the dose was in the hydrogel №5 with peat filler: $\text{BOD} = 0.28 \pm 0.03 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$ decreased to values of $0.3\text{-}3 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$ at SSPH $T_{0.5} = 15.1 \pm 1.6$ years. Higher doses of colloidal silver 100 ppm to suppress the BOD to values of $0.02\text{-}0.07 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$ (with the exception of sample № 2 where the $\text{BOD} = 1.2 \pm 1.6 \text{ g} \cdot \text{m}^{-3} \cdot \text{hour}^{-1}$) and a maximum dose 1000 ppm leads to BOD about 0.01 ± 0.02 , i.e., biological activity here is not statistically significantly different from zero. Calculated value $T_{0.5}$ in this case increases up to 20-70 (144) years.

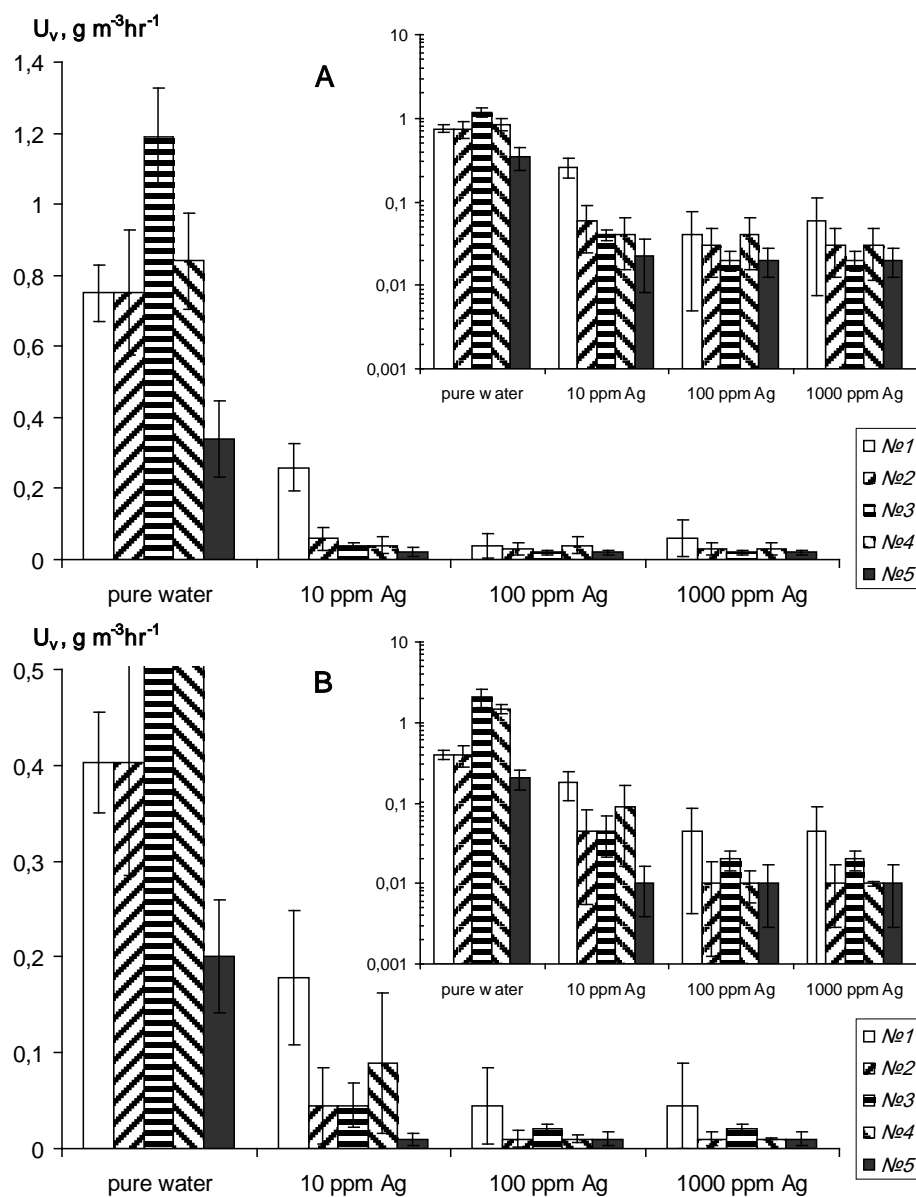


Figure 3. BOD as an indicator of resistance to biodegradation of the hydrogels and their compositions with silver. №№1-4 are different types of hydrogels (see “Materials and methods”); **A** is ionic silver, **B** - colloidal silver; inset is semi-logarithmic scale.

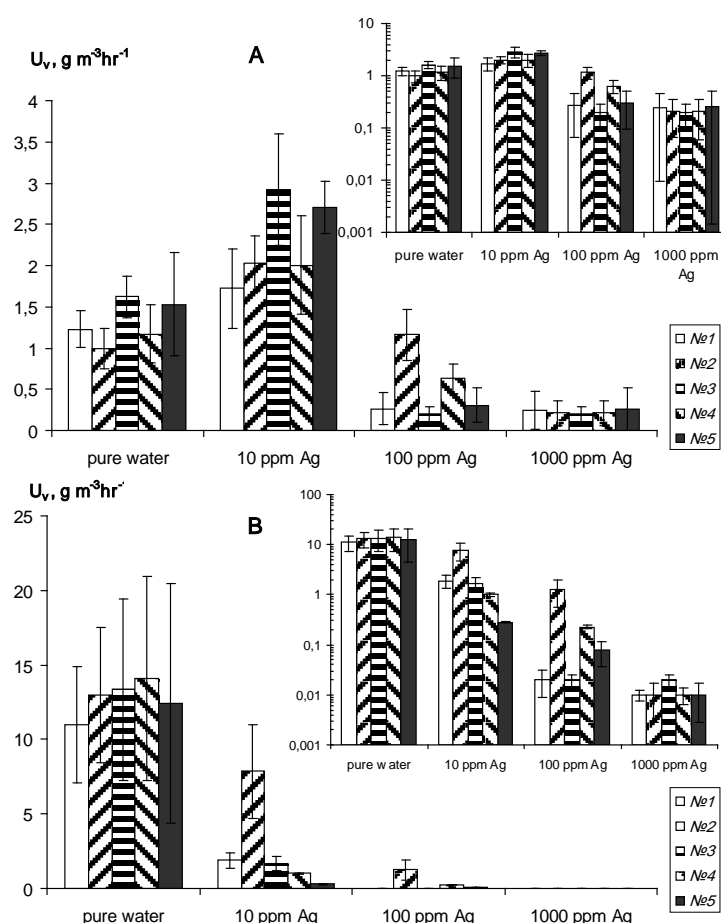


Figure 4. The change in BOD of hydrogels and protective gel compositions with silver in the case of mixing with sandy soil substrate; legend - see Fig. 3

4. Conclusions

Soils provide an extremely important ecological function of the organic matter biodegradation. In order to perform a comparative assessment of this process, we suggested the indices of potential BOD in soils, the techniques for their calculation, based on the modern analysis tools, and developed the grading system for common light-textured soils.

Optimal function of coarse-grained soils with forest floor corresponds to the rates of the potential volume consumption of $10\text{--}40\text{ g}\cdot\text{m}^{-3}\cdot\text{hour}^{-1}$. Normal activity is destabilized at low ($<4\text{ g}\cdot\text{m}^{-3}\cdot\text{hour}^{-1}$) or excessively high ($>80\text{--}100\text{ g}\cdot\text{m}^{-3}\cdot\text{hour}^{-1}$) values of the BOD.

In case of regulated, moderate recreation, the values of potential soil respiration and biodegradation remain within the normal range. Heavy uncontrolled recreational burden leads to destruction of soil cover and suppression of the soil biological activity, decreasing it to low and very low rates ($<2\text{ g}\cdot\text{m}^{-3}\cdot\text{hour}^{-1}$), which is natural only for humusless sub-soil strata and parent rock.

We would recommend a simple and low-cost technique for the evaluation of oxygen consumption by soil samples, incubated in closed flasks, using portable electrochemical gas analyzers, as a promising tool for the assessment of biological activity and biodegradation potential of organic matter in the soil. This method provides more unbiased results, than the traditional ways to esteem respiration

through CO₂ emission, which require adjustments for the interphase processes – gas adsorption and dissolution.

Modern soil conditioners in the form of synthetic polymeric hydrogels based on polyacrylamide and acrylates are susceptible to microbial degradation and are characterized by half-lives of 0.2 to 3.2 years (to 6.8+4.5 years in the case of the SSPH filling by dispersed peat)

The protective composition of the rhizosphere on the basis of hydrogels and silver inhibitors are more resistant to biodegradation if they are not mixed with the soil substrates. Half-lives in them with a small dose of silver in 10 ppm range from 5 to 35 years, and with large doses of 100-1000 ppm can reach 70-100 years and above.

Mixing hydrogel compositions with a mineral soil substrate and putrefactive micro-organisms leads to a sharp increase of biological activity and biodegradation of SSPH; their suppression is possible only when using high doses of silver inhibitors from 100 to 1000 ppm mainly in the colloidal form.

Acknowledgments

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References

- [1] Dale T 1978 Total, chemical and biological oxygen consumption of the sediments in Lindaspollence, Western Norway *Marine Biology* **49** (4) 333-341
- [2] Salem N, Verdonck O, De Boodt M and Timmerman J 1985 Comparative studies on the effect of soil conditioners on the biological activity of organic wastes *Acta Hort. (ISHS)* **172** 99-206
- [3] del Giorgio P and le B. Williams P 2005 Respiration in Aquatic Ecosystems OUP, Oxford, 326
- [4] Advances in Water Resources & Hydraulic Engineering 2009 Tsinghua Univ. Press, 2284
- [5] Parkin T B, Doran J W and Franco-Vizcaino E 1996 Field and laboratory tests of soil respiration In: J W Doran and A J Jones (eds.) Methods for assessing soil quality. *Soil Sci.Soc. Am. Spec. Publ.* **49**. SSSA, Madison, WI 231-246
- [6] Woods End Research 1997 Guide to solvita testing and managing your soil. Woods End Research Laboratory, Inc., Mt. Vernon, ME.
- [7] Smagin A V, Sadovnikova N B and Smagina M V 2014 Biodestruction of Strongly Swelling Polymer Hydrogels and Its Effect on the Water Retention Capacity of Soils *Eur. Soil Sci.* **47** (6) 591–597 doi: 10.1134/S1064229314060088.
- [8] Smagin A V 2012 Theory and practice of soil engineering. Moscow State University Press, Moscow 544 [in Russian]
- [9] Smagin A V 2006 Soil phases; the gaseous phase. In: G. Certini and R. Scalenghe (eds.) Soils: Basic concepts and future challenges. Cambridge Univ. Press, UK Cambridge 75-90
- [10] Ramamoorthy R, Dutta P K and Akbar S A 2003 Oxygen sensors: Materials, methods, designs, and applications *J. of Material Science* **38** 4271-4282
- [11] O'Mahony F C, O'Donovan C, Hynes J, Moore T, Davenport J and Papkovsky D B 2005 Optical oxygen microrespirometry as a platform for environmental toxicology and animal model studies *Environmental Science and Technology* **39** 5010-5014
- [12] Warkentin M, Freese H M, Karsten U and Schumann R 2007 New and fast method to quantify respiration rates of bacterial and plankton communities in freshwater ecosystems by using optical oxygen sensor spots *Applied Environmental Microbiology* **73** 6722-6729
- [13] Budnikov V I, Fedchenko V N, Drobinin D V, Kus'mitsky G E, Sinkin V V, Lokotkov A N, Smagin A V and Nazarov V B 2014 The composite water-holding material and its production method *Patent RU №2536509*, data 27.12.2014