Effect of Organic Matter on Sulfate Reduction Occurring in Alkali (Szik) Soils

É. TIMÁR

Research Institute for Soil Science and Agricultural Chemistry of the Hungarian Academy of Sciences, Budapest

The formation of soda always plays a very important role in the development of alkali soils. Previous observations and recent experiments point to the fact, that both chemical processes, and biological processes are involved in the formation of high pH values in soda affected soils.

As a result of biological processes, soda formation depends on the Na_2SO_4-content of soil, or ground water. In anaerob conditions this compound is reduced by the microorganism *Desulfovibrio desulfuricans*. The metabolic activities of this organism lead to the appearance of Na_2S. As a consequence of hydrolysing processes the reduced sulfur leaves the soil in form of H_2S and the sodium is linked to the carbonates of the soil.

From reports, dating from the second part of the eighteenth century, we know that soda has been extracted from some of the lower lying areas of land that were flooded periodically by water.

These spots of water-covered territories were popularly named "bad smelling lakes" because of the H_2S smell. We can suppose that, in the time before the regulation of the water-ways of the river Tisza, although there were *chemical* processes of soda formation, the conditions for the ***biological*** processes of soda formation were more favourable. Research work began ten years ago in our Institute in connection with this problem. The first results of investigations have shown that, besides other constituents of environmental conditions, organic matter has an important role.

By these experiments the knowledge of the physiology and biochemistry of *Desulfovibrio desulfuricans* was greatly increased. It was determined that this obligate anaerobic organism has a very interesting metabolism.

In the course of its energy-yielding life processes, this microbe is responsible for two reactions: in one molecular H^+ is oxidized to water, and in the other type, H^+ is replaced by some organic compounds (lactate and certain alcohols). During these processes, oxygen is removed from sulfates. It is interesting that in building its body, the microorganism always needs microquantities of some proteins or amino acids.

In the course of our investigations the first aim was to determine the role of the quality and quantity of organic matter in sulfate reduction. A soil profile originating from Sárrét district of Fejér county was selected for analysis. This soil was periodically water-logged and amelioration had not been carried out in the area. Chemical and physical properties of the soil are represented in Table 1.

Conditions, considered as favourable for biological sodium carbonate formation, are present in this soil. Identical quantities (10 g.) of soil previously dried and sieved with 100 ml. of distilled water were placed in flasks. Into the vessels, prepared in this manner, increasing amounts (0.5 g., 1 g., 5 g.) of Na_2SO_4 were added. To some samples Ca-lactate or cellulose (Whatman-1 filterpaper grounded) was added. There were also treatments without organic matter. The flasks were closed with air-tight rubber stoppers into which two

Table 1.

Experimental data of Nagyhörcsög-profile 12, 0—10 cm

I. *Data of ground examination*

pH H_2O	8.2
pH KCl	7.8
$CaCO_3$ %	28.4
Humus %	20.6
Total N %	1.02
C : N	11.5

II. *Aqueous extract*

pH	7.2	
Dry residue	0.920	%
Ignition residue	0.630	%
Soluble humus	0.140	%
Alkali metal alkalinity	1.41	me./100 g. soil
Alkali earth metal alk.	0.62	me./100 g. soil
Total alkalinity	2.03	me./100 g. soil
Cl^-	2.46	me./100 g. soil
SO_4^{2-}	7.33	me./100 g. soil
Anions (total)	11.82	me./100 g. soil
Ca^{2+}	0.96	me./100 g. soil
Mg^{2+}	4.66	me./100 g. soil
Na^+	8.04	me./100 g. soil
K^+	0.26	me./100 g. soil
Cations (total)	13.92	me./100 g. soil

III. *Mechanical composition %*

Hygroscopic water	6.54
Loss in hydrochloric acid processing	33.61
mechanical fraction mm. 1 —0.25	2.68
0.25 —0.05	16.71
0.05 —0.01	13.98
0.01 —0.005	3.64
0.005—0.001	8.69
<0.001	20.69
Physical sand	33.37
Physical clay	33.02
Loss in hydrochloric acid processing	33.61
	100.00

IV. *Exchangeable cations*

	me.	S %
Ca^{2+}	21.71	27.91
Mg^{2+}	42.90	52.16
N^+	12.09	15.54
K^+	1.07	1.37
S	77.77	
T	109.85	

glass-tubes were inserted. With the aid of these tubes N_2 gas was led through the samples. The flasks were connected with receptacles that contained sulfuric-acid mixed with a *copper*-sulfate solution to receive the developing H_2S gas. At the end of the experimental period (99 days), the pH and E_h of the liquid phases of the individual samples, were measured. The amount of H_2S trapped in the receptacles was gravimetrically determined. Subsequently the bound sulfide in the soil was released from the samples with 10 per cent HCl-acid and again collected in copper-sulphate solution, acidified with H_2SO_4.

The data from the above experiments are summarized in Table 2. The data show that the amount of Na_2SO_4 in the soil has a role in the processes of biological sulfate reduction. In samples without organic additions, this influence is striking. With 5 g. of Na_2SO_4 the process is slight and the redox potential decreases, but with 1 g. or 0.5 g. additions the effect is not appreciable. It is very important to notice, that the H_2S production and the development of sulfide containing compounds could only be determined in the presence of organic substances.

The E_h data decreases in a negative direction, and the pH value increases, in all cases where organic matter (Ca-lactate or cellulose) was added.

In evaluation of the data it is very important to note that the process is similar in both cases of organic addition. Soil with only the original organic material present did not influence the processes. From the investigations we can conclude that: the process of biological sulphate reduction is mainly influenced by the quantity of organic matter.

The production of H_2S gas in nature may be the result of several processes: geological aerobic or anaerobic putrefaction, and the metabolism of the facultative anaerob *Desulfovibrio desulfuricans* or similar organisms. As protein-like materials were in low supply in the test soil, the high H_2S production could only be the result of the metabolism of sulfate reducing bacteria.

Table 2.

The pH, E_h and the amount of S^{2-} ions in the soil samples treated

Treatment	E_h	pH	S^{2-} totally as per cent of total given S
5 g. $Na_2SO_4 \cdot 10\ H_2O$			
a) Without organic matter	− 30	8.4	—
b) 0.5 g. Ca lactate	−270	8.9	14.1
c) 0.5 g. cellulose	−230	8.8	12.4
1 g. $Na_2SO_4 \cdot 10\ H_2O$			
a) Without organic matter	+280	8.0	—
b) 0.5 g. Ca lactate	−210	9.0	32.0
c) 0.5 g. cellulose	−196	8.5	21.0
0.5 g. $Na_2SO_4 \cdot 10\ H_2O$			
a) Without organic matter	+300	8.0	—
b) 0.5 g. Ca lactate	−194	8.6	38.0
c) 0.5 g. cellulose	−176	8.7	33.0

This fact was proved by using an isotopic method. It was the marked sulfur of the Na_2SO_4 and not the S of the proteins present in the soil which was released. The data showed that the H_2S was formed mainly from the inorganic sulfur compounds.

The process was very intensive when cellulose was added as the organic amendment. We suppose that the biological sulfate-reduction in the presence of cellulose is the result of metabolism where several anaerobic organisms utilize this material. In this way H_2 gas is also produced. This metabolic product gives one of the fundamental food materials for the life of *Desulfovibrio desulfuricans*.

We supposed further that the H_2S, originating from putrefaction, also plays an important role in the process of biological sulfate reduction. The H_2S from these sources decreases the redox-potential of the environment and the active organisms of this process utilize the oxygen harmful for *Desulfovibrio desulfuricans*.

Влияние органического вещества на процесс восстановления сульфатов, происходящий в засоленных почвах

Е. ТИМАР

Научно-Исследовательский Иститут Почвоведения и Агрохимии А. Н. Венгрии, Будапешт

Резюме

Формирование характера и характерных признаков, а также бесплодия засоленных почв является результатом комплексных процессов, протекающих в почве. В этих процессах играют роль как биологические, так и абиотические факторы. Существенное значение имеет определение роли биологических процессов в засолении, но не только вообще, а фактически, в точно исследованных и правильно описанных случаях.

В ходе исследований нами в модельных опытах вызывалось образование соды и сероводорода в почвах, в которых в условиях Венгрии это явление встречается и в природе. Для опыта взята почва из разреза сделанного в окрестностях Шаррет комитата Фейер. Эта почва временами подвергается затоплению и не была еще мелиорирована. В почве имеются те условия, которые можно считать благоприятными для биологического образования соды. Предварительно высушенные и очищенные от растительных остатков образцы почвы весом в 10 г помещали в колбы, заливали дистилированной водой (по 100 мл). В подготовленные таким образом сосуды добавляли разное возрастающее количество (0,5 г — 1 г — 5 г) $Na_2SO_4 \cdot 10H_2O$. К одной части образцов добавляли лактат-Са, или целлюлозу (молотую фильтровальную бумагу Ватман № 1), в часть вариантов органическое вещество не вносили. Колбы герметически закрывали резиновыми пробками. В пробки были продеты две стеклянные трубки. При помощи этих трубок через колбы пропускали газообразный N_2. Выделяющийся газообразный сероводород улавливался в сосудах, содержащих раствор сернокислого сульфата меди.

По окончании опыта — через 99 дней — определялись pH и Eh жидкой фазы помещенных в колбы образцов.

Количество выделенного сероводорода определяли гравиметрическим методом. Затем связанный сульфид в почвенных образцах выделяли при помощи HCl и улавливали в растворе сульфата меди подкисленном серной кислотой.

Количество внесенного Na_2SO_4 сильно влияет на степень восстановления сульфатов. Выделение сероводорода наблюдалось только в образцах к которым было добавлено органическое вещество. В этих случаях значения окислительно-восстановительного потенциала последовательно были отрицательными, а значения pH сдвигались в сторону щелочности. Выделение сероводорода происходило исключительно в присутствии органического вещества, при этом целлюлоза — как источник углерода — оказывало такое же влияние на ход процесса, как и лактат.

На основе изложенного можно сделать вывод, что биологическое восстановление сульфатов и образование соды в почве зависит от качества и количества органического вещества почвы.