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THE INFLUENCE OF MUNICIPAL SEWAGE AND HUMIC SUBSTANCES ON CALCIUM AND MAGNESIUM CONCENTRATIONS IN RIVERINE WATER

The investigations were carried out with riverine water samples collected from the Odra and its tributary, the Oława. As shown by the results obtained, biochemical degradation of organic pollutants concomitant with biocoagulation phenomena brought about a change in the concentration of calcium and magnesium cations in water, and a new state of calcium–magnesium equilibrium in the double-layer humus complex was established. As a result, calcium concentrations in the riverine water began to vary, but these variations were not substantial. Those processes had an indirect influence on the concentration of magnesium. When after addition of municipal sewage to the water investigated the value of the Ca/Mg molar ratio fell below that of the calcium–magnesium equilibrium in the humus complex, magnesium content decreased in the course of biochemical degradation. But when the Ca/Mg ratio was higher than that of the calcium–magnesium equilibrium, the concentration of magnesium rose. As a result of those processes, the value of the Ca/Mg ratio in the water investigated approached that of the calcium–magnesium equilibrium in the humus complex. The investigations corroborated the ionic character of biocoagulation, because the change in the concentration of calcium and magnesium cations induced by these processes showed an equivalent correspondence with the concomitant change in alkalinity. The results were substantiated by the data of statistical analysis for 6 rivers chosen (189 cross-sections, 10-year period). As shown by these data, magnesium concentrations are described by the function $y = a/x + bx + c$, where $x = \text{Ca/Mg}$, and a, b, c are constants.

1. INTRODUCTION

Calcium and magnesium ions in natural water are amongst the most frequent alkaline-earth metals that occur in the environment. The concentration of the cations in riverine water varies, depending on the geological structure of the catchment area, the system of management, the value of discharge and the processes that occur in the wa-

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ter (including biochemical processes).

Both calcium and magnesium come predominantly from the dissolution of mineral deposits, e.g. dolomites or magnesites, due to the action of precipitation water penetrating the soil. In agricultural areas, generally fed with calcium- and magnesium-containing fertilizers, the infiltrating precipitation water becomes enriched with these cations. In idle land, calcium- and magnesium-enrichment of precipitation water is much poorer, so there are favourable conditions for continuing soil degradation by podsolization as a result of gradual runoff (due to acid precipitation) of calcium, magnesium and humic substances together with the heavy metals accumulating in them [1].

Another factor that affects the concentration of calcium and magnesium in riverine water is a number of processes induced by the discharge of wastewater polluted with organic substances [2]. As a result, there is a decrement in calcium and magnesium content. The phenomena mentioned should be attributed to the biochemical degradation occurring in the water and to the presence of humic substances.

Humic substances are amongst the major components of surface water. They occur in the form of metal–humic acid complexes, mostly Ca–humic acid or Mg–humic acid. The cations are bound in the absorption phase (by functional groups, e.g. carboxylic or phenolic) and in the diffuse layer. For the anticipated calcium and magnesium concentration or for the Ca/Mg molar ratio, the equilibrium state is established in terms of the Donnan equilibrium concept. The ability of the complex to bind calcium and magnesium is pH-dependent; in other words, it also depends on the dissociation of the functional groups.

The calcium–magnesium equilibrium of the complex depends primarily on the calcium and magnesium concentration in the water. In other words, this is such a Ca/Mg molar ratio at which (as it has been found in the Odra and the Oława river water samples) the exchange potentials of the two cations in the humus complex are in equilibrium. When the Ca/Mg ratio value is lower than that of the equilibrium state, the calcium and magnesium cations enter and leave the humic acid complex according to the following sequence:



The energy of the complex decomposition is described by the same sequence in the opposite direction [3]. When the Ca/Mg ratio takes the values greater than those of the equilibrium, the sequence will change, and the calcium cation will be on the left-hand side of the magnesium cation and will display a higher energy of entry and a lower energy of exit than magnesium cation. This phenomenon will be referred to as ‘concentration effect’.

The value of the Ca/Mg ratio at which the calcium–magnesium equilibrium occurs can be determined by a variety of methods. One of these consists in determining calcium and magnesium concentration variations following coagulation with an iron or an aluminium coagulant. It is necessary to repeat coagulation of water sam-

ples at least 10 times in 7-day intervals. Thereafter, the variations of calcium and magnesium content should be related to the value of the Ca/Mg ratio. The equilibrium value is the one at which the decrement and the increment of the cations of interest are minimal [4].

Another method relates the colour intensity of the water and iron concentration (from at least 10 physicochemical analyses in one-week intervals) to the Ca/Mg molar ratio for the water under study. The calcium–magnesium equilibrium point for the humus complex corresponds to the value of the Ca/Mg ratio at which the lowest colour intensity and iron concentration were measured, or to the reflection point of the curves which relate colour intensity and iron concentration to the Ca/Mg ratio (figure 1) [4].

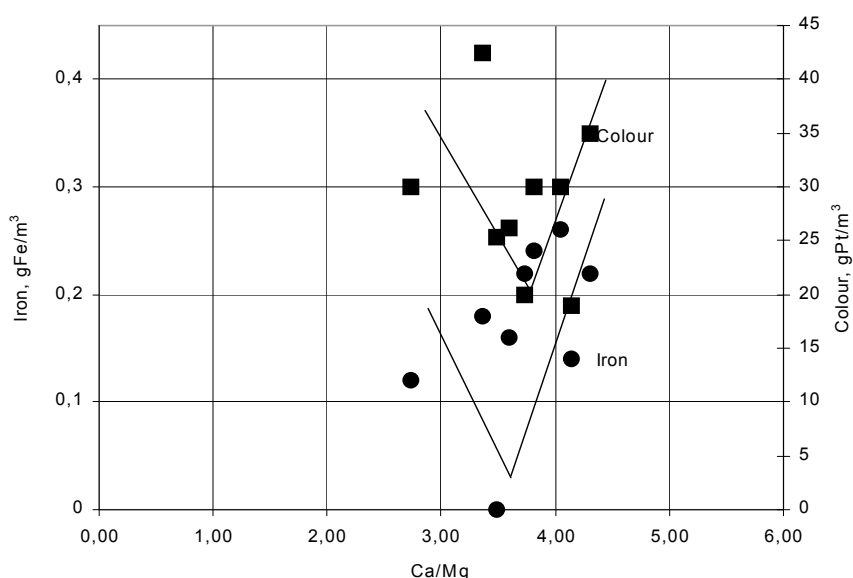


Fig. 1. Effect of Ca/Mg molar ratio on colour intensity and iron concentration (for the Oława)

In another method (which also involves at least 10 physicochemical analyses in one-week intervals), average molar or normal calcium and magnesium concentrations and thereafter the Ca/Mg molar ratio are calculated. The value of the Ca/Mg ratio obtained via the above procedure is approximately equivalent to the equilibrium value (table 1) [5]. Thus, for the Odra river the Ca/Mg ratio value at which the calcium–magnesium equilibrium *A* occurs ranges from 2 to 3 and for the Oława river it exceeds 3.5 [4]. The investigated riverine water showed a higher affinity for magnesium than for calcium cations [5].

Table 1

Average calcium and magnesium concentrations as well as Ca/Mg equilibrium values

| Origin of water samples | Average concentration, deg. of hard. | | Ca/Mg molar ratio | Experimental values of Ca/Mg equilibrium | Period of study |
|--|--------------------------------------|------|-------------------|--|-----------------|
| | Ca | Mg | | | |
| The Odra | 10.00 | 4.57 | 2.18 | 2.20 | 03 to 05 1991 |
| Infiltration water and the Oława water | 12.27 | 3.22 | 3.81 | 4.00 | 03 to 06 1991 |
| The Odra | 8.31 | 4.23 | 1.96 | 1.95 | 01 to 03 1998 |
| The Odra | 9.30 | 4.30 | 2.81 | 3.00 | 03 to 05 1996 |
| The Odra | 9.20 | 3.60 | 2.55 | 2.55 | 01 to 03 1998 |
| The Oława | 15.00 | 4.0 | 3.72 | 4.00 | 07 to 10 1998 |
| The Oława | 14.57 | 4.10 | 3.55 | 3.60 | 03 to 07 1999 |
| The Odra | 8.01 | 3.33 | 2.40 | 2.40 | 03 to 07 1999 |
| The Odra | 10.23 | 4.73 | 2.16 | 2.15 | 10 to 12 1999 |
| The Odra | 8.87 | 3.68 | 2.43 | 2.50 | 08 to 09 2000 |

2. METHODS

The experiments were carried out with riverine water samples collected from the Odra (263 km from the source) and from its tributary the Oława (1 km from the Oława and the Odra confluence). The samples (of a 10 dm³ volume each) were treated with municipal sewage (after one-hour sedimentation) in varying amounts (0; 0.75 dm³; 1.50 dm³). Tap water-based samples treated with natural humic substances and municipal sewage as well as with CaCl₂ or MgSO₄ were also investigated. The samples prepared via the above route were aerated at a constant temperature and a rate of 3.0 dm³/h for 15–21 days. Every 48 hours, after sedimentation, samples were taken for physicochemical analysis to determine organic matter concentration (BOD₅, COD_p and TOC), calcium and magnesium content and hardness. Both rivers investigated did not much differ in the levels of organic pollutants. Humic acid concentrations varied from 2 to 7 g/m³ and coloured matter content ranged between 15 and 80 g/m³.

3. RESULTS

One of the major processes that occur in polluted water is biochemical degradation of organic substances. As a result, the number of bacteria, which initially increase (e.g., in the aerated Odra water samples (10 dm³ + 1.5 dm³ of municipal sewage) up to 63·10⁵/cm³), begin to decrease dramatically following biocoagulation (down to 15·10³/cm³ in the same sample) (figure 2). Biocoagulation, which generally was initiated after 48 hrs of aeration, brought about not only a substantial decrement in the

number of bacteria, but also a considerable removal efficiency for organic matter (up to 85%) and cations (Me^{2+}) binding to organic complex.

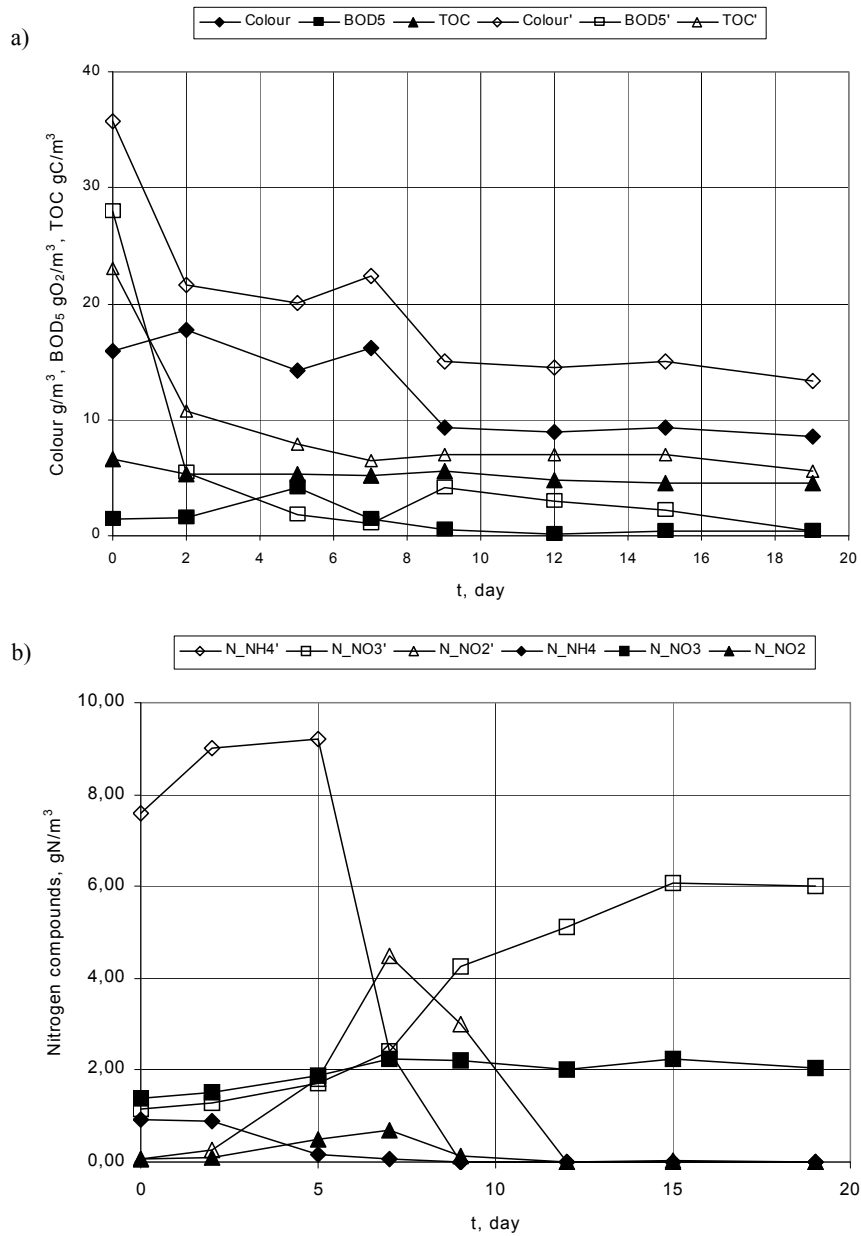


Fig. 2. Colour, BOD, TOC (a) and nitrogen concentration (b) versus time in aerated water of the Odra river (samples treated with 1.5 dm³ of municipal sewage)

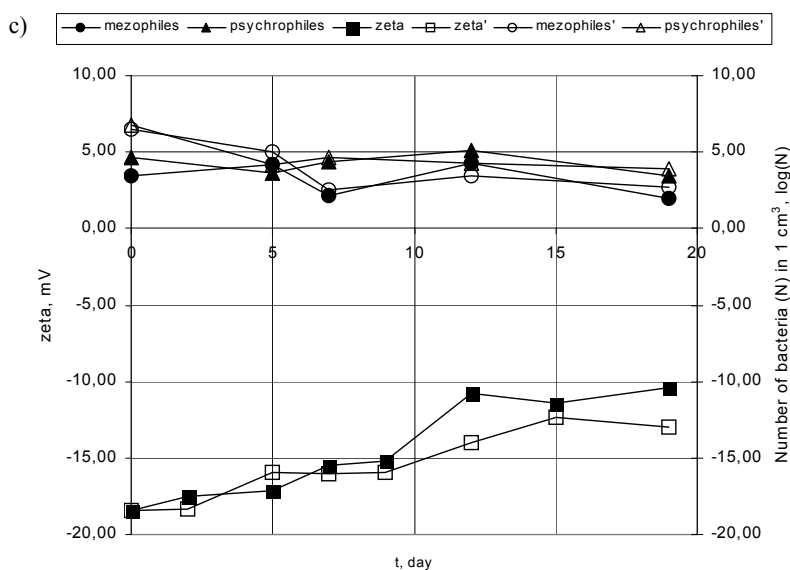


Fig. 2. Zeta potential versus time in aerated water of the Odra river (samples treated with 1.5 dm³ of municipal sewage)

Other biochemical processes that occur in polluted water can be itemized as follows: ammonification, nitrification, and (less frequently) denitrification in the near-bottom zone. As a result of ammonification, the concentration of ammonia nitrogen was found to increase mostly after 48 or 120 hrs of aeration (the Odra river sample in figure 2b). The nitrification process involved two stages with a considerable rise in the concentration of nitrites (figure 2b, with a maximum after 7–9 days of aeration) at the first stage, and a considerable rise in the concentration of nitrates in the second stage. The processes mentioned were concomitant with relevant calcium and magnesium concentration, as well as with a decrease in the zeta potential value (which dropped from –18.4 mV to –13.0 mV in the sample mixed with municipal sewage, figure 2c).

4. PHYSICOCHEMICAL PHENOMENA INVOLVED IN BIOCHEMICAL DEGRADATION

The biocoagulation process that runs in an aquatic environment is associated with a number of physicochemical phenomena, which occur on the surface of bacterial cell membranes. Bacteria growing in polluted water have the ability to bind cations, especially those of calcium and magnesium, to the polysaccharide cell walls, owing to the production of bonds with carboxylic groups and phosphatic groups at low pH and high pH, respectively. Besides the processes of Me^{2+} cation binding also sorption takes place.

As a result, net total surface charge density at higher calcium concentration takes positive values [7], [8], and the resulting zeta potential is also positive. Hence, the binding process occurs on the surface of both bacteria and humic substance, as well as on any other pollutants with a negative zeta potential. And there is also sorption of pollutants on the surface of destabilized bacteria agglomerates. The biocoagulation process is paralleled by a slight variation in the zeta potential despite a considerable removal of pollutants (figure 2). This is an indication that humic acids and other polluting species are bound to the surface of positively charged bacterial cells, thus forming a negatively charged organic complex. In that way, the chemical biodegradation process contributes to the removal of divalent cations from the solution (figure 2).

Depending on the calcium and magnesium concentration established by adding municipal sewage or an inert calcium or magnesium salt to the Odra and the Oława water samples in the course of biochemical degradation, the value of the Ca/Mg ratio increased or decreased (figure 3, aerated samples collected from both the rivers). Colour intensity decreased and so did BOD₅. In the control samples (with no addition of municipal sewage), calcium and magnesium concentrations as well as the Ca/Mg ratio varied only slightly.

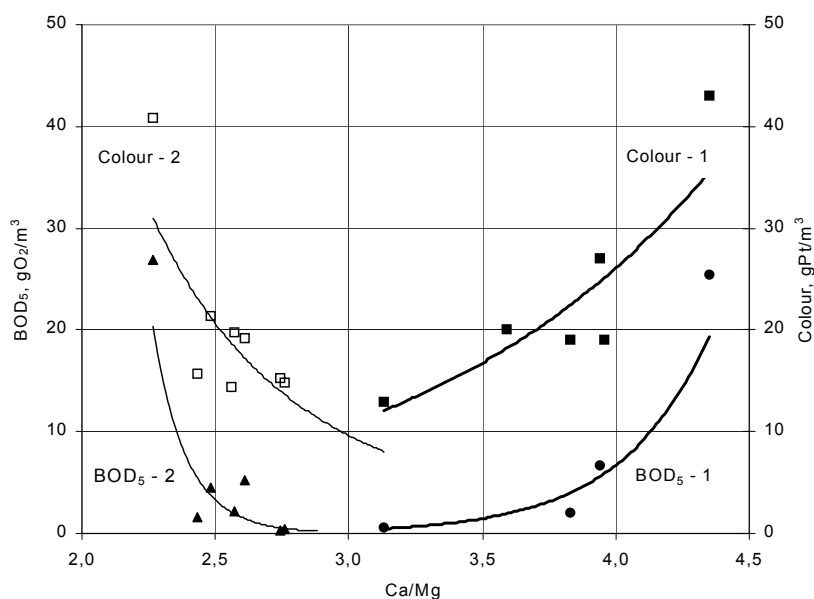


Fig. 3. Effect of Ca/Mg molar ratio on BOD₅ and colour intensity in aerated water of the Oława river
 (1 – the Oława water + 1.5 dm³ of municipal sewage + 9 mg of Mg/dm³,
 2 – the Oława water + 1.5 dm³ of municipal sewage)

The variations of the Ca/Mg ratio in the course of biochemical degradation should

be attributed to the physicochemical properties of the humic substances and to the calcium–magnesium equilibrium established in the humus complex or rather in the organic complex.

If following municipal sewage addition the Ca/Mg ratio takes values lower than that of the equilibrium, the decrement in divalent cations (Me^{2+}), i.e. those of calcium and magnesium, as a result of bacterial growth will equalise (in terms of the Donnan principle) the concentrations of both cations in the diffusion layer of the organic complex with the concentration of the solution. Hence, the cations of a higher exit energy (i.e. Ca^{2+}) will be released, thus decreasing the value of the Ca/Mg ratio in the diffusion layer. Consequently, the Mg^{2+} cations enter the adsorption layer of the complex, and the Mg^{2+} cations will also leave the solution and enter the diffusion layer of the complex until the state of equilibrium has been achieved. The number of magnesium cations which entered the complex corresponded equivalently to the ratio of the concentration of the calcium cations that left the adsorption layer to the equilibrium Ca/Mg molar ratio ($\text{Ca/Mg} = A$). That is why calcium concentration in the water remains stable or slightly decreases, magnesium concentration generally decreases (figure 4), and the Ca/Mg ratio increases. As a result, the net total surface density of the organic complex charge decreases, and so does the stability of the complex, which is indicated by the decrease in colour density (figure 3).

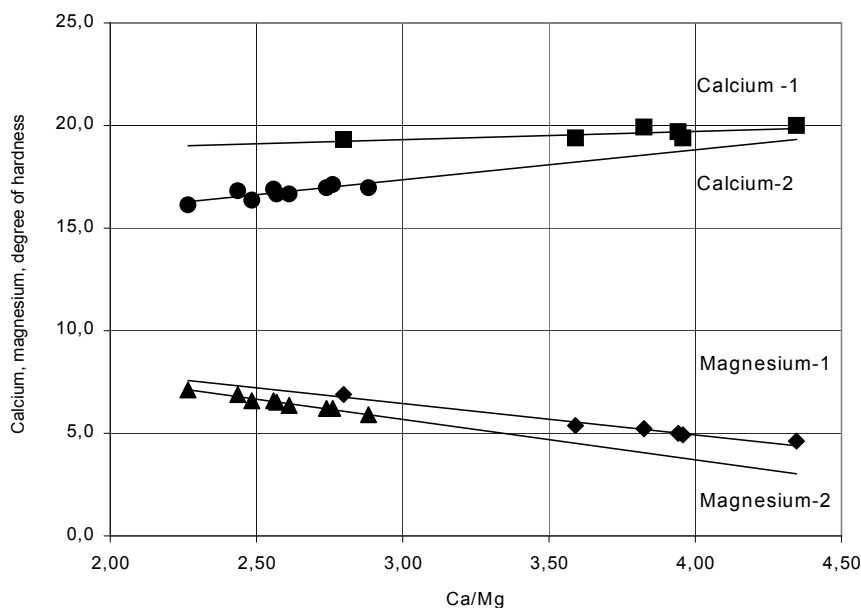


Fig. 4. Effect of Ca/Mg ratio molar on calcium and magnesium concentrations in aerated water of the Oława river
(1 – the Oława water + 1.5 dm³ of municipal sewage + 10 mg of Mg/dm³,

2 – the Olawa water + 1.5 dm³ of municipal sewage)

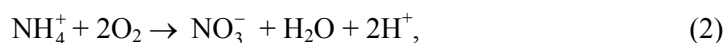
If after addition of municipal sewage the Ca/Mg ratio takes the values higher than that of the equilibrium, the decrement of calcium and magnesium in the water due to bacterial growth will make the magnesium cations leave the complex, which is in agreement with the Donnan principle and with the concentration effect. Thus, in the water, magnesium concentration will increase and the Ca/Mg ratio value will decrease. When magnesium cations leave the diffuse layer, there will be a concomitant increase of the Ca/Mg ratio values, which will probably make the calcium cations pass from the diffuse layer to the adsorption layer of the complex. Consequently, there will be a decrement of the surface charge density, which deteriorates the stability of the complex (a response to both phenomena is a decrease in colour intensity) (figure 3).

The stabilisation of the calcium–magnesium equilibrium in the complex resulting from the calcium and magnesium decrement produced by the biodegradation process indicates that the value of the Ca/Mg molar ratio varies in the course of the process to approach the equilibrium value. This happens irrespective of whether the Ca/Mg ratio stabilises below or above the equilibrium value after addition of municipal sewage. The calculated value of the Ca/Mg ratio (on the basis of average measured calcium and magnesium concentrations) approaches that of the equilibrium (table 1).

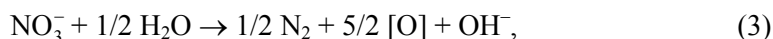
5. PHYSICOCHEMICAL PHENOMENA CONCOMITANT WITH BIOCOAGULATION

The processes, which occur in water, are connected with these that occur in the sludge deposited on the bottom as a result of biocoagulation. The sludge biochemical processes release calcium and magnesium to water which next are bounded to organic complex. These processes are responsible for rather low content of these cations in the organic fractions of sludge after aeration (Mg²⁺, 0.5–1.6%, Ca²⁺, 3.2–8.7%). It is much less than the value of decrement, for example, of magnesium after biocoagulation (figure 2). This process caused also a decrease in alkalinity. The alkalinity, in general, is influenced by biochemical changes of nitrogen compounds [9]:

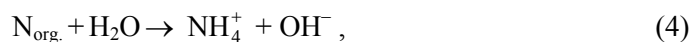
- nitrification which runs according to equation (2) [5] produces an alkalinity decrease of 0.142 mval/1 mg N_{NH₄⁺}:



- denitrification which proceeds according to equation (3) brings about an alkalinity increase of 0.071 mval/1 mg N_{NO₃⁻}:



- ammonification which follows equation (4) results in an alkalinity rise of 0.071 mval/1 mg N_{org} :



- incorporation, i.e. binding of ammonia nitrogen by growing biomass, according to equation (5) contributes to an alkalinity decrement of 0.071 mval/1 mg $N_{\text{NH}_4^+}$:

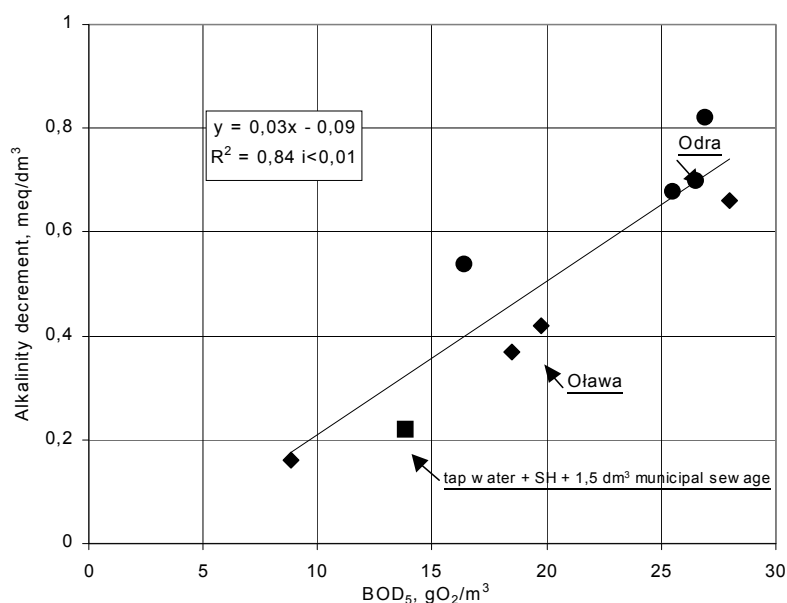


Fig. 5. Effect of BOD₅ on alkalinity decrement due to biocoagulation in aerated riverine water samples

If we balance the alkalinity variations induced by the conversion of nitrogen compounds (nitrification, denitrification, incorporation of ammonia nitrogen, ammonification), it will be possible to determine – by taking into account the difference between initial (after addition of municipal sewage) and final (after termination of the process) alkalinity – the BOD₅-related decrement in alkalinity which results from the binding of Ca^{2+} and Mg^{2+} cations by the biomass. This linear relationship allows the alkalinity variations to be correlated quantitatively with the BOD₅ load. Relevant values obtained in our study averaged 0.04 meq/mg BOD₅ (figure 5). And this substantiates a close relation between the course of the biocoagulation and the kinetics of biochemical degradation. As mentioned earlier, the decrement of cations produced by biocoagulation is concomitant with some phenomena, which should be attributed to the properties of humic substances, i.e. with the stabilisation of the calcium and magnesium cation equilibrium in the double-

layer complex. And this process is associated either with the decrement or increment of magnesium. The resulting variations in equivalent Mg^{2+} concentration and the decrement in alkalinity are generally similar (figure 6).

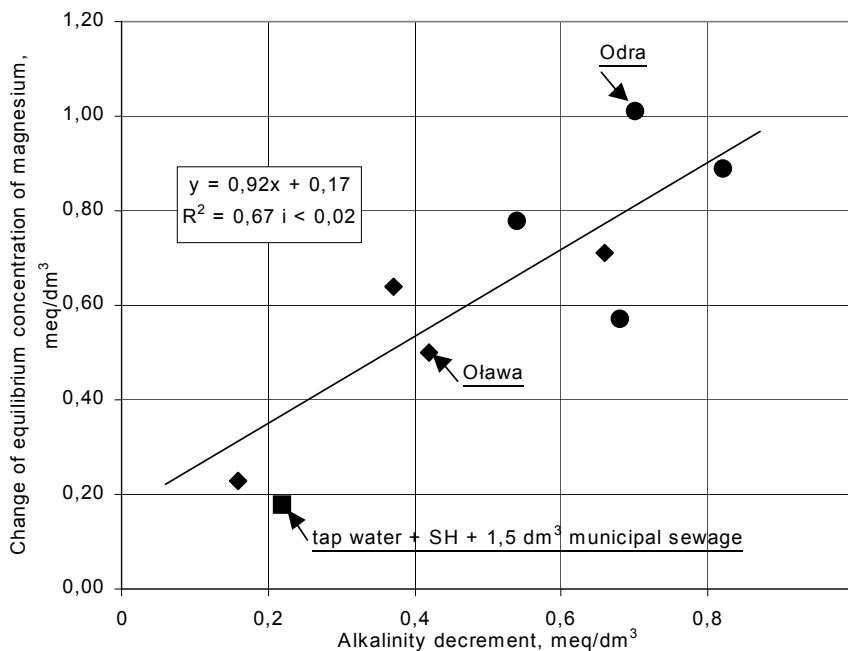


Fig. 6. Effect of alkalinity decrement due to biocoagulation on the equilibrium concentration of magnesium in aerated riverine water

Analysis of magnesium variations (mostly with the tendency to decrease) as a function of BOD_5 removal in the several rivers of our choice revealed the value which ranged from 0.027 to 0.36 meq Mg^{2+} /mg BOD_5 (table 2) [5].

Table 2

Effect of BOD_5 decrement on the variations of magnesium concentration in cross-sections chosen

| River | $\frac{\Delta Mg^{2+}}{\Delta BZT_5}$ meq/mg O_2 |
|-----------------------|--|
| The Biała Głuchołaska | 0.027 |
| The Kaczawa | 0.104 |
| The Nysa Kłodzka | 0.027 |
| The Nysa Szalona | 0.083 |

| | |
|-----------|----------------|
| The Oława | 0.059 to 0.306 |
| The Odra | 0.039 to 0.357 |

6. STATISTICAL ANALYSIS OF CONCENTRATION VARIATIONS OF CALCIUM AND MAGNESIUM IN POLISH RIVERS OF OUR CHOICE

In order to verify the results of laboratory tests, statistical analysis was carried out for BOD₅, calcium and magnesium variations as a function of the Ca/Mg molar ratio. Relevant data were obtained from the Institute of Meteorology and Water Management, Wrocław. The above factors were analyzed in the water of the following rivers: the Vistula (11 cross-sections), the Odra (10 cross-sections), and the tributaries of our choice to both the rivers (the Nysa Łużycka, the Warta, the Ina and the Bug with 1 cross-section each). The data covered the time span of 1988–1999 and were collected in the cross-sections of 189 rivers. The results of statistical analysis corroborated those of the laboratory tests. Positive correlations of the relationship $Mg = f(Ca/Mg)$ (significance level $\alpha \leq 0.01$, correlation coefficient $r > 0.6$, number of measuring sites $n > 20$) were established for over 90% of the 189 cross-sections analysed within 10 years. In the majority of instances, the relation $Mg = f(Ca/Mg)$ was described by the following curve (figure 7):

$$y = \frac{a}{x} + bx + c, \quad (6)$$

where $x = Ca/Mg$, a , b , c are rare constants, and y stands for Mg^{2+} concentration in mg/dm^3 . However, in some cases the relation in question is linear

$$y = ax + b, \quad (7)$$

where x , y , a , b have the same notation as above.

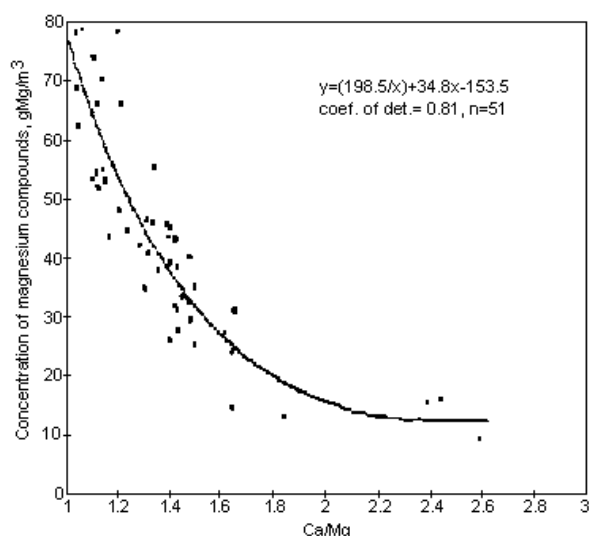


Fig. 7. Effect of Ca/Mg molar ratio on magnesium concentration in the Vistula water (63.7 km from the source)

Accepting the above assumptions, a positive correlation for the relation $\text{Ca}^{2+} = f(\text{Ca/Mg})$ was obtained only in approximately 26% of cases, and this is in agreement with the results of laboratory tests. The proportion of positive correlations for $\text{BOD}_5 = f(\text{Ca/Mg})$ approached 9%, mainly for polluted water samples.

7. SUMMARY

As shown by the results of the study, calcium and magnesium concentrations in the polluted water tested were influenced by the biochemical biodegradation process in water and the sludge deposited at the river bottom as a result of biocoagulation. The change in concentration of metal cations (Me^{2+}) (with a rate approaching 0.045 meq/mg BOD_5) brought about a new state of cation equilibrium in the double-layer humus substances in organic complex and in the water. As a result, calcium concentration underwent certain (but not considerable) variations. The process mentioned above had an indirect influence on the concentration of magnesium. When after addition of municipal sewage the value of the Ca/Mg molar ratio stabilised below the calcium–magnesium equilibrium value in the complex, the concentration of magnesium decreased in the course of biochemical degradation. But when following wastewater addition the Ca/Mg ratio took values greater than that of the equilibrium, magnesium concentration increased. As a result, the value of the Ca/Mg molar ratio in the water tested was in the range of that of the calcium–magnesium equilibrium in the

complex. Statistical analysis of the data obtained for several Polish rivers of our choice within 10 years showed that in over 90% of the 189 cross-sections investigated magnesium concentration depended on the Ca/Mg molar ratio described by the function $y = a/x + bx + c$. Calcium concentration was positively correlated with the Ca/Mg ratio only in 26% of instances.

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WPLYW ŚCIEKÓW MIEJSKICH ORAZ SUBSTANCJI HUMUSOWYCH NA STĘŻENIE WAPNIA I MAGNEZU W WODACH PŁYNĄCYCH

Badania wód Odry i Oławy wykazały, że procesy biochemicznego utleniania wprowadzonych zanieczyszczeń organicznych oraz towarzyszące im zjawiska biokoagulacji zmieniały stężenia kationów wapnia i magnezu. W wyniku tych procesów ustalał się nowy stan równowagi wapnia i magnezu w warstwie podwójnej kompleksu humusowego. W następstwie tych zjawisk stężenie wapnia w badanych wodach wahało się, lecz nie ulegało zasadniczym zmianom. Procesy te wpływają pośrednio na stężenie magnezu. Jeżeli w wyniku wprowadzenia ścieków do wody wartość stosunku molowego Ca/Mg ustaliła się poniżej stosunku równowagowego wapnia i magnezu, to w kompleksie humusowym stężenie magnezu malało w miarę postępu procesów biochemicznego rozkładu. Natomiast w przypadku, gdy wartość tego stosunku była większa od równowagowego, stężenie magnezu rosnęło. W wyniku tych procesów wartość stosunku molowego Ca/Mg w badanych wodach wahała się w granicach wartości równowagi wapniowo-magnezowej kompleksu humusowego. Badania potwierdziły jonowy charakter biokoagulacji, gdyż zmiana stężenia kationów wapnia i magnezu wywołana tymi procesami odpowiadała równoważnikowo związanej z nią zmianą zasadowości. Wyniki te potwierdziła analiza statystyczna dla wybranych

6 rzek (189 przekrojów z 10 lat). Wykazała ona, że stężenie magnezu opisuje funkcja $y = a/x + bx + c$, gdzie $x = \text{Ca/Mg}$, a , b , c są stałe.