Application of the buffer theory for evaluating attenuation and natural remediation of ionic pollutants in aquatic ecosystems

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Abstract

The main focus in this review is showing how to use the developed buffer theory for assessing and predicting the long-term phenomena of attenuation and natural remediation of ionic pollutants in contaminated aquatic ecosystems, as well as for analyzing the way by which metals move and transform within the environment, the distribution of metals in ecosystems, their deposition and cycling in the terrestrial environment. The buffer theory is based on the rigorous thermodynamic analysis of complex chemical equilibria under environmental conditions in aquatic ecosystems, as natural waters and soils. It has been established that both homogeneous and heterogeneous systems manifest a buffer action towards all their components. The buffer properties in relation to the solid phase components are amplified with an increase of solubility due to protolytic or complex formation equilibria in saturated solutions. It has been established that the buffer capacities of components are mutually proportional, whereas for heterogeneous systems these relationships depend on the stoichiometric composition of solid phases. The use of the developed buffer approach may yield extended knowledge and a deeper understanding of the processes that control the concentrations of components. A number of the important conclusions concerning the investigated buffer systems have been made. The obtained results are indented to provide researchers with a tool needed to help them to set reliable limits of ion (metal) levels in the environment.

Keywords: Buffer capacity, Ecosystem, Heterogeneous multicomponent system, Proportionality relation between buffer capacities

Introduction

Risk assessment of heavy metals in ecosystems

The basic requirements of the Ecological Risk Assessment (ERA) for metals are as follows: the chemical species of the metal in the environment, environmental conditions affecting those species as well as the presence of receptors of potential concerns (Chapman et al. 2003; Williams 2005; Povar 2011).

To understand the control of metal solution concentrations in ecosystems, one needs to understand the removal processes for involving compounds and phases (Povar 1996a, b, c; Povar and Spinu 2013a, b, c; Spinu and Povar 2013c). From the point of view of

Homo polluens (the human impact on ecosystems), what matters among the characteristics of the environment is its resistance to change, its homeostasis, and its buffering processes (Spinu and Povar 2013d; Povar and Spinu 2015b, 2014b). In chemical terms, the problem is to understand how and by how much the composition of the environment will change for a given input.

Risk assessment must consider the complexity of metal speciation in the environment, transformations, and interactions between different metals and metal species and between metal binding phases in soils and sediments (Povar 1999, 2000b; Povar and Luca 2003). These factors all affect bioavailability (Adriano et al. 2002). In addition, ERA of metal-contaminated sediments needs to consider the three separate

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possible transformation processes for metals in the aquatic environment: solubilization (= increased bioavailability), association with sediments (= decreased bioavailability), and resolubilization (= increased bioavailability) (Fishtik and Povar 2006; Povar and Fishtik 2009; Povar and Spînu 2012, 2014a).

For a risk assessment of contaminated sites, or for natural attenuation process management, it is of primary importance to know how and to what extent the contaminants will spread or decline in the future. On the other hand, the problem of controlling the ion concentrations in natural systems may be formulated as follows: What is the response of the system when changing the parameters that govern the pM (negative logarithm of metal activity)? In other words, what is the pM buffer capacity of the system? Here $pM = -\log[M]$, where $[M]$ is the equilibrium concentration of the metal ion M^{n+}, analogically, as $pH = -\log[H^+]$ (Povar 1998a; Povar et al. 2009c).

Although chemical analytical measurements are necessary to investigate the composition and magnitude of sediment contamination and to identify possible contaminant sources, these determinations, alone, are inadequate tools for fully characterizing and predicting potential biological effect. Having only this information, it is impossible to predict the future development of the metal amounts and its species in contaminated ecosystems under the change of environmental conditions (e.g., pH, Eh[1], cations, organic matter and other metal-complexing ligands) (Stumm and Morgan 1996, Povar and Spinu 2014a).

Mathematical modeling of the buffer action of aquatic ecosystems using computer technologies

In view of the increasing anthropogenic impact on aquatic ecosystems, our concern increases about the occurrence of some irreversible and undesirable changes. The tasks regarding the prediction and assessment of aquatic ecosystems' quality along with the determination of its resistance to anthropogenic impacts come out, as the ability to restore itself is not unlimited. For aquatic ecosystems—buffer open dynamical systems, associated with environmental flows of matter and energy, the ecosystem stability can be defined as its ability to come back to initial states after external disturbances, maintaining the productive function in the socio-economic system. For the modern ecological sciences, the mathematization of research is a general trend. If before the application of mathematics in ecological science was limited to the use of statistical methods for the analysis and treatment of experimental data, now it is more emphasis on mathematical modeling using computer technology. These days, the specialists in the field of natural sciences need to learn how to answer the questions: "How to make a quantitative assessment of the effects of external (including anthropogenic) impacts on ecosystems or how to get the scenarios for the development of natural systems?" For assessments and forecasts on the development of natural systems in time, a mathematical model of the process is essential.

Natural attenuation/intrinsic chemical remediation of metals and buffer capacity of ecosystems

The term "natural attenuation" refers herein to chemical processes that, under favorable conditions, act without human intervention to reduce the concentration of contaminants in soil and ground water (Christensen et al. 2000; Murtaza et al. 2011). The natural processes, however, can be accelerated by adding to the soil inexpensive amendments that is cost effective and minimally invasive. Because of their immutable nature, strict processes alone may not be successful in mitigating the risks from metals at sites. Accelerating these processes, i.e., *accelerated natural remediation* that ultimately immobilizes the metals might be a viable option. For instance, the applications to soils of certain amendments as lime and phosphates can enhance key biogeochemical processes in soils that eventually immobilize metals so increasing their buffer properties (Bright et al. 2000; Islam et al. 2001; Thornton et al. 2001). The materials incorporated into contaminated soils speedup and optimize, in the case of metals, their immobilization as mediated by the processes such as precipitation, complexation, and redox reactions (Povar and Spinu 2014a; Povar et al. 2014).

The capacity of buffer systems to oppose (resist) to the variation of their composition (usually to pH changes) by influence of external fluxes of chemical compounds of natural or anthropogenous character, that shift chemical equilibria, is called buffer property, and its efficiency—buffer action. The buffer action of aquatic ecosystems is one of its fundamental physico-chemical characteristics. In the case of soils, the buffer action composes of the buffer action of a set of mineral and organic components and presented by solid, liquid, and gaseous compounds. The buffer capacity of soils in relation to chemical compounds is defined by the content of chemical elements in the soil solution (the parameter of intensity) and on the content of mobile compounds of these elements in solid phases (the parameter of capacity). The buffer capacity of soils can be discovered by the fact that the increase of amounts of toxic metals is not accompanied by an increase of their content in plants; the different buffer action of the soils in relation to one element is manifested in unequal toxic concentrations

for plants. The same soil can possess different buffer action in relation to different metals.

The relationship between buffer capacity and the ability of clays to retain Pb in interactions between Pb contaminant leachate and the clays was studied in (Yong et al. 1990) using a natural clay from Quebec and laboratory-prepared clays (kaolinite, illite, and smectite). The retention of Pb in the clay suspensions by increasing amounts of acid was investigated and the results examined in terms of the buffer capacity of the clays. As the clays receive increasing amounts of acid, it has been established that high amounts of Pb can be retained if the buffer capacity prevents the pH from dropping to values where precipitation mechanisms are not operative. The high carbonate content in the illite gave it a higher buffer capacity than the smectite and natural clay and permitted it to retain high amounts of Pb. The authors (Yong et al. 1990) proved that high Pb uptake by the clays could affect the buffer capacity and the Pb retention capacity. In the paper (Yong and Phadungchewit 1993), it has been demonstrated that high amounts of heavy metals are retained in the soils if the soil buffer capacity remains high enough to resist a change in pH. The results from the selective sequential extraction analysis of heavy metals supported also the conclusion of the significance of soil buffer capacity with regard to heavy-metal retention (Yong and Phadungchewit 1993). The capacity of the soils to retain high amounts of heavy metals as they receive increasing amounts of acid (i.e., as the pH is reduced) depended directly on the soil initial pH values and on their buffer capacities.

In this paper, the use of thermodynamic and computer modeling in heterogeneous multicomponent systems "mineral-soil solution" is examined. In a number of published works, the methods for solving the problems of shift from chemical-analytical, descriptive characteristics of the systems to the quantitative study of their chemical equilibria by thermodynamic and computer modeling have been described. These processes include the heterogeneous interaction of minerals and soil solution, homogeneous reactions of hydrolysis and complex formation, as well as the acid-base, redox, buffers, and other important soil properties. Despite numerous studies of soil solutions in natural and laboratory conditions, many questions of their composition and transformation, as well as assessment of anthropogenic impacts and forecasting natural processes, remain unresolved. The development of our understanding on the relationship of processes and their quantitative assessment, based on thermodynamic equations of chemical equilibria, allows in many considered cases to replace the time-consuming determination of total content and mobile forms of chemical

elements on easily measured pH values, the analytical (total) concentration of components, etc. In the general form, the provision of plants is assessed by two indicators:

1) The potential of chemical element (nutrient potential)—an energy characteristic, defined as the change in the Gibbs energy of the reaction
2) The potential buffering capacity of soils in relation to the elements of plant nutrition. The smaller the ion activity changes as conditions change, the higher the buffering capacity of the soil, the more stable conditions of plant nutrition. In this review, under the original approach developed by authors, both indicators are analyzed for a number of real heterogeneous multicomponent systems "mineral-soil solution".

Review

Chemical thermodynamic concepts and laws have been applied for developing the theory of complex chemical equilibria in multicomponent heterogeneous systems and its practical application use under real, non-standard conditions in a number of papers (Povar 1996a; Povar and Fishtik 2009; Povar and Rusu 2012; Spinu and Povar 2013a, Spinu and Povar 2013b, Povar and Spinu 2015a). Computing of global change in Gibbs energy for a set of chemical equilibrium equations in multi-species and multiphase chemical systems has been performed in the cited papers. Their authors have been applying the criterion of the intensity of buffer action for the systems, containing liquid and solid phases, and developed the theory of mechanism of buffer action in two-phase buffers.

The metal buffer processes in natural systems

The ability of the metal immobilization is called buffering capacity. Without buffering capacity, soil metal concentrations would change rapidly. At elevated concentrations when the influx of metals exceeds the metal buffer capacity, toxic effects may occur (Chapman et al. 2003). On the other hand, for essential metals, there is a risk of deficiency when the bioavailability is very low.

The buffer processes are of crucial importance within the concepts of the risk assessment controlling and the natural attenuation. The concept of buffering is closely related to controlling the chemical composition of systems and the removal processes (Fishtik and Povar 2006; Povar 1995). Any buffer system has a certain potential reserve, which controls equilibrium and keeps one of the equilibrium parameters (equilibrium concentrations) constant.

Sediments are one of the most important sink and buffer reservoir for metals, metalloids, and other
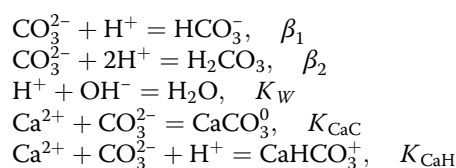
contaminants that reduces their bioavailability but which also retains contaminants for future potential exposure. The sediment metal concentration and sediment-water chemistry (metal binding phases in sediments, pH, Eh, ligands, etc.) control free metal ion activity in aqueous solutions by the processes of formation-dissolution of the solid phases and the re-actions of complex formation. Metal binding phases in sediments reduce metals' availability and hence exposure. In contrast, complexation by ligands may enhance metal mobilization but often lowers bioavail-ability. The lack of information about the metal buffer properties of ecosystems can be explained by the ab-sence of the quantitative theory that may predict their buffer behavior. The low buffer capacity of ecosys-tems, that are unable to preserve a constant pM, can lead to disastrous environmental consequences.

Homogeneous (mono-phase) ion buffer systems

In the previous works (Povar 1995; Povar 1998b), we have introduced the concept of stability coefficients for characterizing the buffer properties of ternary systems. A valuable relation between the temperature coeffi-cients of the logarithms of the equilibrium component concentrations and the stability coefficients has been found (Povar 2000a; Povar and Spinu 2015c, d). The applicability of the obtained expressions for controlling the chemical composition of the multicomponent systems and for model solutions with a desired temperature dependence of the concentration for one of the components has been discussed. The higher the stability coefficient, the higher is the response of the system to a change in the equilibrium parameter (the concentration) of one of the components.

The buffer action of homogeneous metal buffer sys-tems is based on complexation reactions. The ligands, capable to bind the metals, thus, reducing their con-centrations, appear to be a part of the resistance mechanism. The presence of excess ligand may fix the concentration of free metal ions at some value. If an additional amount of metal is added to the buff-ered solution, its concentration will be changed only slightly. This action is analogous to the acid-base buffer, and hence solutions containing an excess of chelating agent can be regarded as "metal buffers". These theoretical relationships provide a deeper insight into the mechanism of buffer action, of ion buffer systems based on the complexing, competitive reactions (Povar and Spinu 2014e, f).

Further, the homogeneous system "$Ca^{2+} - CO_3^{2-} - H_2O$" will be analyzed. Here, the following complex formation reactions in solution are possible (Povar et al. 2014; Spinu and Povar 2013a):

$$
\begin{aligned}
CO_3^{2-} + H^+ &= HCO_3^-, \quad \beta_1 \\
CO_3^{2-} + 2H^+ &= H_2CO_3, \quad \beta_2 \\
H^+ + OH^- &= H_2O, \quad K_W \\
Ca^{2+} + CO_3^{2-} &= CaCO_3^0, \quad K_{CaC} \\
Ca^{2+} + CO_3^{2-} + H^+ &= CaHCO_3^+, \quad K_{CaH}
\end{aligned}
$$

For this system, three mass balance equations can be written:

$$
\begin{aligned}
C_{Ca}^0 &= [Ca^{2+}] + [CaOH^+] + [CaCO_3^0] + [CaHCO_3^+] \\
C_{CO_3}^0 &= [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] + [CaCO_3^0] + [CaHCO_3^+] \\
C_H^0 &= [H^+] - [OH^-] - [CaOH^+] + [CaHCO_3^+] + [HCO_3^-] + 2[H_2CO_3]
\end{aligned}
$$

$$(1)$$

For convenience, the following concentration func-tions will be used:

$$
\begin{aligned}
\varphi_1 &= [H] + [OH] + [CaOH] + [CaHCO_3] + [HCO_3] + 4[H_2CO_3] \\
\varphi_2 &= -[CaOH] + [CaHCO_3] \\
\varphi_3 &= [CaHCO_3] + [CaCO_3] + 2[H_2CO_3] \\
\varphi_4 &= [CaCO_3] + [CaHCO_3] \\
\varphi_5 &= [HCO_3] + 2[H_2CO_3] + [CaHCO_3]
\end{aligned}
$$

$$(2)$$

The equation for calculating the buffer capacity to-wards proton, calcium, and carbonate can be derived (Spinu and Povar 2013a):

$$
\begin{aligned}
\beta_H &= \varphi_1 + \frac{\varphi_2\varphi_4\varphi_5 - \varphi_2^2 C_{CO_3}^0 + \varphi_2\varphi_3\varphi_4 - \varphi_3\varphi_5 C_{Ca}^0}{C_{Ca}^0 C_{CO_3}^0 - \varphi_4^2} = \\
&= \frac{C_{Ca}^0 C_{CO_3}^0 \varphi_1 - \varphi_1\varphi_4^2 + \varphi_2\varphi_4\varphi_5 - \varphi_2^2 C_{CO_3}^0 + \varphi_2\varphi_3\varphi_4 - \varphi_3\varphi_5 C_{Ca}^0}{C_{Ca}^0 C_{CO_3}^0 - \varphi_4^2}
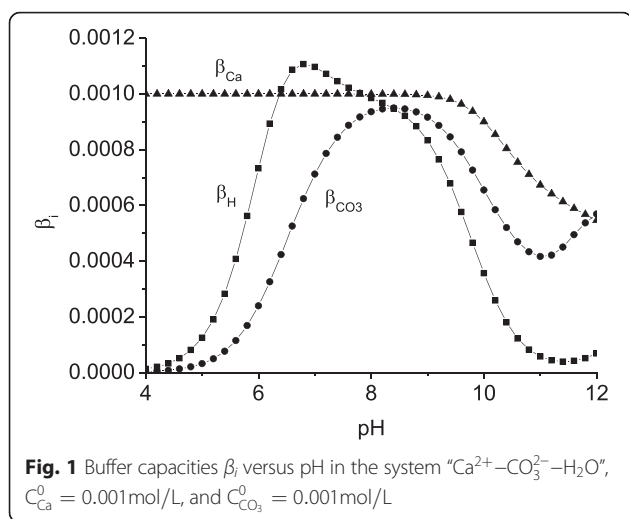\end{aligned}
$$

$$(3)$$

$$
\begin{aligned}
\beta_{Ca} &= C_{Ca}^0 + \frac{\varphi_2\varphi_3\varphi_4 - C_{CO_3}^0 \varphi_2^2 + \varphi_2\varphi_4^2\varphi_5 - \varphi_1\varphi_4^2}{C_{CO_3}^0\varphi_1 - \varphi_3\varphi_5} = \\
&= \frac{C_{Ca}^0 C_{CO_3}^0\varphi_1 - C_{Ca}^0\varphi_3\varphi_5 + \varphi_2\varphi_3\varphi_4 - C_{CO_3}^0\varphi_2^2 + \varphi_2\varphi_4\varphi_5 - \varphi_1\varphi_4^2}{C_{CO_3}^0\varphi_1 - \varphi_3\varphi_5}
\end{aligned}
$$

$$(4)$$

$$
\begin{aligned}
\beta_{CO_3} &= C_{CO_3}^0 + \frac{\varphi_2\varphi_3\varphi_4 - \varphi_1\varphi_4^2 - C_{Ca}^0\varphi_3\varphi_5 + \varphi_2\varphi_4\varphi_5}{C_{Ca}^0\varphi_1 - \varphi_2^2} = \\
&= \frac{C_{Ca}^0 C_{CO_3}^0\varphi_1 - C_{CO_3}^0\varphi_2^2 + \varphi_2\varphi_3\varphi_4 - \varphi_1\varphi_4^2 - C_{Ca}^0\varphi_3\varphi_5 + \varphi_2\varphi_4\varphi_5}{C_{Ca}^0\varphi_1 - \varphi_2^2}
\end{aligned}
$$

$$(5)$$

The dependences of the buffer capacities towards proton, carbonate, and calcium on pH, calculated by Eqs. (3)-(5), are depicted in Fig. 1. It is worthy to note that the maximal values of β_i do not strongly differ from each other.

Heterogeneous (two-phase) ion buffer systems

Buffering action is not only intrinsic to homogeneous solutions. These properties are possessed also by

Fig. 1 Buffer capacities β_i versus pH in the system "$Ca^{2+}-CO_3^{2-}-H_2O$", $C_{Ca}^0 = 0.001\,mol/L$, and $C_{CO_3}^0 = 0.001\,mol/L$

heterogeneous systems, i.e., in systems with several phases. The heterogeneous equilibrium causes the specificity of these buffers with respect to mono-phase buffers; the pM at which the buffer capacity is maximum, namely the pM range of the buffer action, can be changed by varying the amount of the second phase.

The theory of the equlibria, properties, mechanism of action, and buffer capacity of the two-phase buffers has been developed by us (Povar 2000a, b; Povar and Luca 2003). In these works, we developed theoretical relationships for the main buffer characteristics. The buffer capacity of the two-phase buffer is considerably greater than that of a single-phase buffer in the pM range around their maximum values (Povar 1996a, b, c, 2000b). We have found that the buffering properties relative to the ions of the sediment are enhanced by side protolytic or complexing reactions occurring in the aqueous solutions. A simple method has been developed to evaluate the buffer action based on the tabulated solubilities of low-soluble compounds.

Despite the abundant information on various buffers, the theory of buffer action has been extensively developed only for homogeneous pH buffers (particularly for the mixtures of conjugate acids and bases). No systematic investigations of buffer properties of heterogeneous (two-phase) buffer systems are available, except a few reports (Povar 1995, Povar 1996a, b, c, 2000a, b). The oldest buffers described in the literature are mono-phase acid-base buffer systems (Fernbach and Hubert 1900; Povar and Luca 2003; Povar 2000b) in respect to pH. These pH buffers are described in detail (Butler 1991; Perrin and Dempsey 1974; Stumm and Morgan 1996).

The ion buffer capacity of heterogeneous (two-phase) systems has been studied relatively well only for the pH buffers (Pfendt 1995; Dougherty et al. 2006), partly because slow reactions make experimental studies difficult, partly because of the mathematical complexity of the theoretical calculations. Most pertinent to the research proposed here is our own result (Fishtik and Povar 2006; Povar 1995, a, Povar 1996b, c, 2000a, b; Povar and Luca 2003, Povar and Spînu 2014e). Those studies dealt with developing metal-ligand buffer capacity theory both for homogeneous and heterogeneous multicomponent systems.

As a criterion for quantitative assessment of the intensity of buffer action of the studied multicomponent heterogeneous systems, one can use the value of the buffer capacity β_i^S (the superscript index "S" specifies the presence of solid phases), which can be defined as a partial derivative
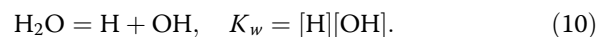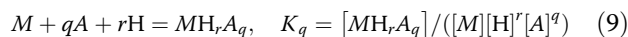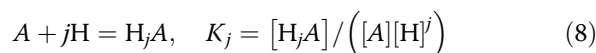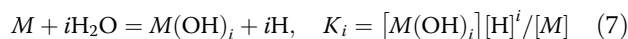
$$\beta_i^S = \left(\frac{\partial C_i^0}{\partial \ln[i]}\right)_{C_j^0(j\neq i)}$$

where C_i^0 and $[i]$ denote the initial (analytical) concentration in mixture and equilibrium concentration of the component "i" of solid phase; correspondingly, at the same time, the subscript index shows that the initial concentrations of other components of the mixture are maintained constant.

We will examine the process of formation of the sparingly soluble salt of arbitrary stoichiometric composition $M_mA_{n(S)}$ (M—metal ion, A—anion of salt):

$$M_mA_{n(S)} = mM + nA, \quad K_S = [M]^m[A]^n. \quad (6)$$
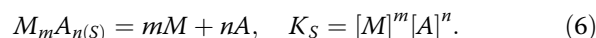
The following set of possible simultaneous reactions in the saturated solution is taken into account:

$$M + iH_2O = M(OH)_i + iH, \quad K_i = [M(OH)_i][H]^i/[M] \quad (7)$$

$$A + jH = H_jA, \quad K_j = [H_jA]/\left([A][H]^j\right) \quad (8)$$

$$M + qA + rH = MH_rA_q, \quad K_q = [MH_rA_q]/([M][H]^r[A]^q) \quad (9)$$

$$H_2O = H + OH, \quad K_w = [H][OH]. \quad (10)$$

For the sake of simplicity, the charges of species are omitted. Near to the reaction equations, the corresponding equilibrium constants are specified.

The mass balance (MB) conditions in this system are formulated by the following equations:

$$C_M^0 = \Delta C_M + C_M^r = \Delta C_M + \sum_{i=1}\sum_{j=0} i\left[M_i(OH)_j\right] + \sum_{q=1}\sum_{r=0}\left[MH_rA_q\right]$$

$$(11)$$

$$C_A^0 = \Delta C_A + C_A^r = \Delta C_A + \sum_{l=0}[H_lA] + \sum_{q=1}\sum_{r=0} q\left[MH_rA_q\right] \quad (12)$$

$$C_H^0 = [H]-[OH] + \sum_{l=1} l[H_lA] - \sum_{i=1}\sum_{j=1} j\left[M_i(OH)_j\right] + \sum_{q=1}\sum_{r=1} r\left[MH_rA_q\right]$$

$$(13)$$

The quantity C_i^r represents the residual concentration in solution of the ion "i", e.g., the total concentration of all the species, containing a given ion, while ΔC_i is its molar quantity in the solid phase in 1 L of solution (Povar 1996a, 2000b; Povar and Spînu 2012; Povar and Spinu 2013a, b, c). In Eq. (13), C_H^0 denotes the excess of H⁺ ions in relation to hydroxyl ions in two-phase mixtures $\left(C_H^0 = -C_{OH}^0\right)$. The square brackets designate the equilibrium concentrations of species in solution.

From the stoichiometric composition of the solid phase, the following ratio is obtained:

$$\frac{\Delta C_M}{m} = \frac{\Delta C_A}{n} \quad \text{or} \quad \Delta C_A = \frac{n}{m}\Delta C_M. \quad (14)$$

On the basis of the written equations, it is possible to deduce the formulas for calculating the buffer capacity in relation to any component of the mixture (Povar and Spinu 2013a):

$$\frac{\beta_A^S}{n^2} = \frac{\beta_M^S}{m^2} \quad (15)$$

For the buffer capacity in relation to the metal ion, β_M^s, the following expression has been obtained:

$$\beta_M^s = \varphi_3 - \frac{\varphi_1^2}{\varphi_2}, \quad (16)$$

where φ_1, φ_2, and φ_3 denote the concentration functions:

Similarly, it has been proven that, for the buffer capacity towards proton, the following expression is valid:

$$\left(\frac{\partial C_H^0}{\partial \ln[H]}\right)_{C_M^0, C_A^0} \equiv \beta_H^S = \varphi_2 - \frac{\varphi_1^2}{\varphi_3}. \quad (18)$$

For the buffer capacity towards the anion of the solid phase, one can deduce:

$$\beta_A^S = \frac{n^2}{m^2}\varphi_3 - \frac{n^2}{m^2}\frac{\varphi_1^2}{\varphi_2} = \frac{n^2}{m^2}\left(\varphi_3 - \frac{\varphi_1^2}{\varphi_2}\right) = \frac{n^2}{m^2}\beta_M^S. \quad (19)$$

The relations (15)-(19) could be obtained on the basis of the MB Eqs. (11)-(13), where the contributions of solid phases are explicitly expressed.

The following remarkable conclusion follows: the buffer capacities towards different components are reciprocally proportional, while the buffer capacities in relation to the ions of the solid phase are interconnected through its stoichiometric coefficients. It is worthy to mention that the obtained relations are only valid in the presence of the mineral (solid phase) $M_mA_{n(S)}$. The thermodynamic stability area of the latter is determined by the value of the Gibbs energy of the overall process (6)-(10):

$$\Delta G_{S,\text{tot}} = -mRT \ln\frac{C_M^r}{C_M^0} - nRT \ln\frac{C_A^r}{C_A^0}, \quad (20)$$

where the quantity C_i^r represents the residual concentration in solution of the ion "i", e.g., the total concentration of all the species, containing a given ion, while ΔC_i is its molar quantity in the solid phase in 1 L of solution. The solid phase is stable if $\Delta G_{S,\text{tot}} > 0$. The condition $\Delta G_{S,\text{tot}} > 0$ corresponds to the beginning of its dissolution and (or) sedimentation. The analysis of the derived equations shows that the buffer capacities β_i^S grow with the increase of the precipitate solubility, e.g., by rising the residual concentration of the component of minerals.

In the case of formation of poorly soluble oxyhydroxides of the stoichiometric composition $M(OH)_{n(S)}$,

$$\varphi_1 = \sum_{i=1}\sum_{j=0} ij\left[M_i(OH)_j\right] + \frac{m}{n}\sum_{l=1} l[H_lA] - \sum_{q=1}\sum_{r=1} r\left[MH_rA_q\right] + \frac{m}{n}\sum_{q=1}\sum_{r=1} rq\left[MH_rA_q\right]$$

$$\varphi_2 = [H] + [OH] + \sum_{l=1} l^2[H_lA] + \sum_{q=1}\sum_{r=1} r^2\left[MH_rA_q\right] \quad (17)$$

$$\varphi_3 = \frac{m^2}{n^2}\sum_{l=0}[H_lA] + \sum_{q=1}\left(\frac{m^2q^2}{n^2} - 2\frac{mq}{n} + 1\right)\sum_{q=1}\sum_{r=1}\left[MH_rA_q\right] + \sum_{i=1}\sum_{j=0} i^2\left[M_i(OH)_j\right].$$

$MOOH_{(S)}$, or $M_2O_{n(S)}$, the following remarkable relation has been derived (Spinu and Povar 2013a):

$$\frac{\beta_H^S}{n^2} = \frac{\beta_M^S}{1^2} \qquad (21)$$

The analysis of the derived equations shows that the buffer capacities β_i^S grow with the increase of the precipitate solubility, e.g., by rising the residual concentration of the component of minerals.

An example of real natural system that we examined is "*Gibbsit—saturated aqueous solution*" (Povar and Rusu 2012). As it is known, the equilibrium concentration of the metal ion is controlled primarily by the soil composition, namely, by one of the most stable soil minerals. Their identification is realized either by thermodynamic calculation or on the basis of known experimental data. For instance, the $[Al^{3+}]$ content in the soil in the range of pH values (6.0 <pH <8.5) is mainly regulated by gibbsite $Al(OH)_{3(S)}$. For a complete picture, it was necessary to consider the hydrolysis reaction of aluminum ions with formation of hydroxy complexes, complex formation reactions with inorganic (fluoride, sulfate, phosphate) and organic ligands, etc. By increasing the acidity in aqueous solutions, the content of aluminum grows quickly due to the interaction of the gibbsite with an acid:

$$Al(OH)_{3(S)} + 3H^+ \Leftrightarrow Al^{3+} + 3H_2O, K_S = [Al^{3+}][H^+]^{-3}$$
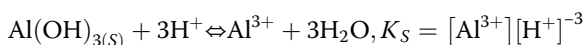
An important interrelation between the buffer capacities of the heterogeneous system "*Gibbsite $Al(OH)_{3(S)}$—saturated aqueous solution*" can be identified:

$$\beta_H^S = 9\beta_{Al}^S \qquad (22)$$

The following composition of the heterogeneous system has been used for the calculations: $C_{Al}^0 = 1°10^{-4}$ mol/L, $C_F^0 = 5°10^{-6}$ mol/L, $C_{Org}^0 = 1°10^{-4}$ mol/L, $C_{PO_4}^0 = 1°10^{-4}$ mol/L, $C_{SO_4}^0 = 1°10^{-4}$ mol/L and $C_{CO_3}^0 = 1°10^{-3}$ mol/L. One can state that the influence of H^+ in the studied pH interval may be neglected, and the OH^- ions exercise influence on β_H^S only at pH >8.5. The aluminum ions and their hydroxocomplexes make a significant contribution in acid solutions up to pH 5.5 and at pH >8 because of the predominance of the stable anionic hydroxocomplex $Al(OH)_4^-$. The results of the calculations of the buffer capacities β_H^S as a function of pH for different compositions of the heterogeneous mixture are shown in Figs. 2 and 3. Therefore, soils in equilibrium with minerals, containing heavy metal ions, have a certain reserve potential, by which the equilibrium is governed, maintaining constant one of
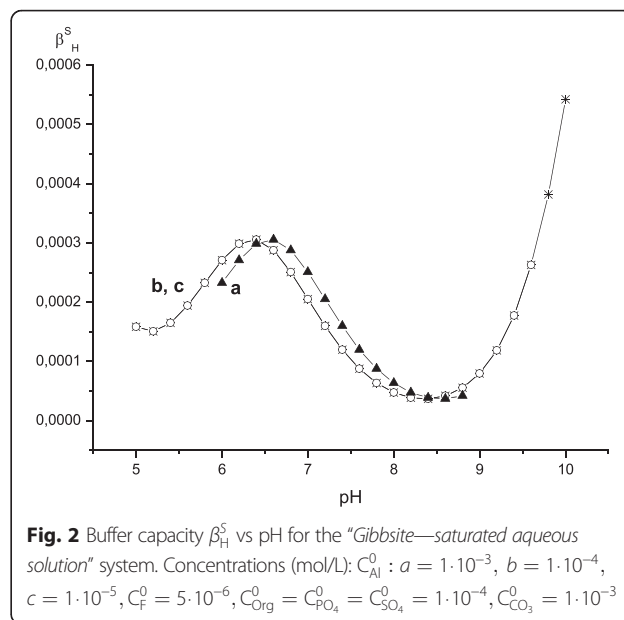
Fig. 2 Buffer capacity β_H^S vs pH for the "*Gibbsite—saturated aqueous solution*" system. Concentrations (mol/L): C_{Al}^0 : $a = 1\cdot10^{-3}$, $b = 1\cdot10^{-4}$, $c = 1\cdot10^{-5}$, $C_F^0 = 5\cdot10^{-6}$, $C_{Org}^0 = C_{PO_4}^0 = C_{SO_4}^0 = 1\cdot10^{-4}$, $C_{CO_3}^0 = 1\cdot10^{-3}$

its parameters, including the equilibrium concentration of heavy metal ions. Thermodynamic analysis of the obtained relations showed that the presence of inorganic and organic ligands, which form stable complexes with ions of the solid phase, enhances the buffer effect of heterogeneous systems.

It has been established that the aquatic ecosystem in equilibrium with minerals has a certain reserve potential, by which the equilibrium is governed and one of its parameters is maintained constant (Povar and Rusu 2012). By means of the presented above equations, the
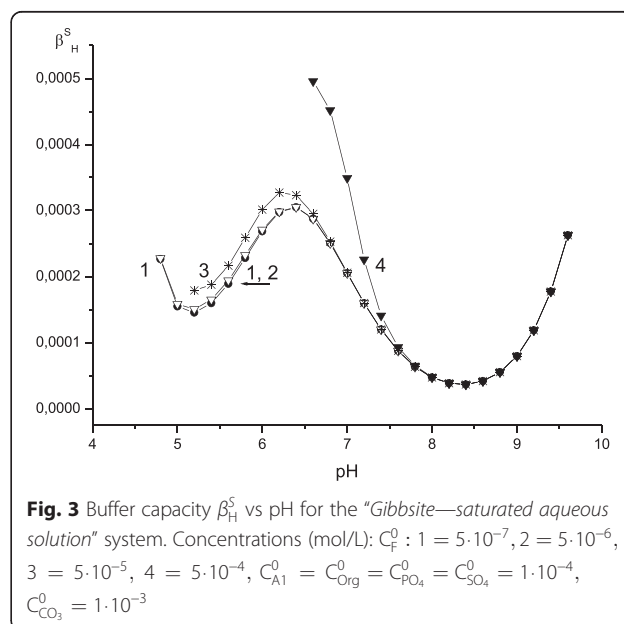
Fig. 3 Buffer capacity β_H^S vs pH for the "*Gibbsite—saturated aqueous solution*" system. Concentrations (mol/L): C_F^0 : $1 = 5\cdot10^{-7}$, $2 = 5\cdot10^{-6}$, $3 = 5\cdot10^{-5}$, $4 = 5\cdot10^{-4}$, $C_{Al}^0 = C_{Org}^0 = C_{PO_4}^0 = C_{SO_4}^0 = 1\cdot10^{-4}$, $C_{CO_3}^0 = 1\cdot10^{-3}$

influence of different factors (temperature, pH and concentrations of main aquatic ecosystem components) on the values of buffer capacities of investigated heterogeneous systems has been studied (Povar and Spinu 2014b). Is has been established that aquatic ecosystem in equilibrium with minerals has a certain potential reserve, by means of which the equilibrium is adjusted and one of its parameters is maintained constant. The presence of ligands which form stable complexes with ions of the solid phase promotes the amplification of the buffer actions of heterogeneous systems. The presented approach can be used for research of the buffer action in the case of formation of one or several other solid phases in natural waters.

The importance of buffer capacity as a geochemical factor of their resistance to pollution and a valuable environment resource must be recognized, and its preservation must be a major component of long-term aquatic system protection policies.

Soil buffering is an integral indicator reflecting the quantitative and qualitative states of the soils, a factor of their stability. The soil system, being a polyfunctional heterogeneous system, comprises solids—minerals, the saturated aqueous—soil solution (liquid phase) and gas phase. Natural soil buffering is caused by a large number of chemical reactions between the aqueous soil solution and particulate minerals. Soil solution in equilibrium with the mineral phases not only accumulates the geochemically mud components but also acts as a natural buffer that controls the transfer of chemical elements and compounds and has the ability to reduce the negative impact of pollutants on plants and animals (Samohvalova et al. 2014).

The paper (Fateyev et al. 1999) established a regular relationship between the content of heavy metals in the soils of different genesis and their buffering capacity towards pH. The authors (Povar and Rusu 2012) proved that soils are buffered with respect to the activity of heavy metal ions, that is $pM = -\log \gamma_M [M] = -\log a_M$ where a_M is the activity of metal ion, and $[M]$ is its equilibrium concentration. Concomitantly there was found a mutual proportionality of buffer capacities towards pH and pM, mentioned above. This remarkable pattern just explains the dependence of the heavy metal ions in soils on their buffering properties towards pH of the soil solution. In other words, the soils are buffered not only towards the hydrogen ion concentration, but also with respect to the concentrations of other dissolved components of soil solutions, including heavy metal ions.

Like the base or acid pH neutralization capacity, the ion buffer pM capacity is mainly represented by the solid aquifer matrix, while the driving force or component is introduced into the solution. This concept has to be seen within the environmental context. It means that only possible and relevant chemical processes should be included. Precipitation appears to be the dominant process of metal immobilization in the presence of anions such as sulfate, carbonate, hydroxide, and phosphate, especially when the concentrations of ions are high. The partition of the depositions of metals in sediments is a natural process that, over the long term, controls their concentrations in aquatic environments. One of the critical factors in assessing long-term potential for effects in aquatic environments is the flux of metal from water to sediments and vice versa.

The use of the buffer approach may yield extended knowledge and a deeper understanding of the processes that control the concentrations of components as well as a powerful tool for the assessment and prediction of long-term effects in natural attenuation as a remediation alternative within contaminated environmental systems.

Within the context of the proposed approach, we intend further to examine the thermodynamics of the coexistence of solid phases, determine the condition under which solids involving common constituents can coexist at equilibrium (Povar and Spinu 2014a; Adriano et al. 2002), the acid-base equilibria, mineral equilibria, and inorganic and organic complexation. It is expected that applying the methodology outlined above, the buffer capacity approach will provide a suitable method to estimate whether or not the pM will change appreciable under "external" influences.

Conclusions

The thermodynamic study within the described buffer approach allows and explains the following:

1) To extend our mechanistic comprehending of natural processes and of accelerate natural processes that may attenuate certain contaminants in groundwater via complex formation (chelating) and precipitation reactions
2) To predict and identify the exact conditions and to what extent these processes are reversible
3) Improve basic understanding of ecological mechanisms and processes
4) Presence of ligands that form stable complexes with ions of the solid phase promotes the amplification of the buffer actions of the heterogeneous systems
5) Presented approach can be used for research of the buffer action in the case of formation of one or several other solid phases in natural waters
6) Use of results of this research allows predicting the variations of the composition and response of the environment at the technogenic loads increasing

7) On the basis of the method of residual concentrations, the original mathematical expressions for the quantitative estimation of buffer capacities towards both components of the mineral phase have been deduced

8) Quantitative basis of the theory of buffer action for heterogeneous systems has been stated. It is established that buffer properties in relation to components of the solid phase amplify with the increase of the solubility. The buffer capacity of any component is a complex function of the equilibrium composition of multicomponent heterogeneous systems.

9) It is proved that the buffer capacities of components are mutually proportional and for heterogeneous systems these relations depend on the stoichiometric composition of the solid phases (minerals)

10) Use of the results of this research allows predicting the variations of the composition and response of the soil environment at the technogenic loads increasing

Overall, the proposed approach is intended to determine the dominant processes that are responsible for observed changes in contaminant concentrations at a site and provide researchers with the knowledge needed to set reliable limits of ion (metal) levels in the environment.

Endnote

[1]$Eh = -2.3 \frac{RT}{F} (\log a_{\bar{e}})$, where F is the Faraday constant and $a_{\bar{e}}$ is the electron activity.

Authors' contributions
IP carried out the theoretical study, analysis, and interpretation of data and drafted the manuscript. OS was involved in obtaining the computational data, participated in the manuscript design, and helped to draft the manuscript. All authors, IP and OS, read and approved the final manuscript.

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