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RESEARCH

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Influence of the interaction of calcium carbonate particles with surfactants on the degree of water pollution in small rivers

Petru Spataru¹, Francisco Fernandez², Joseph W. Sista³, Tudor Spataru³, Oxana Spinu¹ and Igor Povar^{1*}

Abstract

Introduction: The influence of the interaction of calcium carbonate (CaCO₃) and surface-active substances (SAS; surfactants) with different chain lengths and cationic and anionic hydrophilic centers has been analyzed.

Results: Laboratory simulations indicate reduced negative influences on cationic SAS nitrification/self-purification processes in the presence of anionic species. This suggests the role of complex ionic formation [anionic SAS * cationic SAS] as a cause of this effect. UV-Vis spectra of lauryl sulfate (LS) and of cetyltrimethylammonium (CTMA), as well as of their mixtures in ratios of 2:1 and 1:1, treated by fine particles of CaCO₃, display decreased amounts of SAS in analyzed solutions and their presence on the surface of CaCO₃ nanoparticles. UV-Vis spectra reveal the decomposition of the complex [anionic SAS (SAS-An) * cationic SAS (SAS-Ct)] in solutions when CaCO₃ is added. CTMA can be bonded by LS through hydrophobic chains, on the surface of CaCO₃ particles. Therefore, CaCO₃ modifies the nature of LS and CTMA interactions. This leads to an increased degree of toxicity of cationic SAS in aquatic environment. The amounts of CTMA in aqueous solutions are diminished in the presence of ammonium ion NH₄⁺ (2 mg/L). In the presence of two orders higher concentration of ammonium ion, this effect strongly increases, making the association obvious. The structure of cationic SAS does not influence this effect. The obtained results have been confirmed both by timed natural aquatic sample analysis and laboratory simulations using water from Moldovan small rivers (Isnovat, Raut, and Bic).

Conclusions: UV-Vis spectra and laboratory simulations demonstrate the change due to the addition of calcium carbonate. Simulations and laboratory tests of water samples from Isnovat, Bic, and Raut Rivers, establish the cationic SAS negative influence on treatment and self-purification processes.

Keywords: Anionic and cationic surface-active substances, Calcium carbonate, Small rivers, Cetyltrimethylammonium, Lauryl sulfate, Tetrabutylammonium, Toxicity, Water pollution

Introduction

Toxic surfactants from pesticides that have polluted natural sources of water have become a serious problem in recent decades (Lechuga et al. 2016; Thomas et al. 2009). It is known that the presence of surfactants in water can also lead to the solubilization of other oil-soluble pollutants such as DDT and trichlorobenzene (Scott and Jones 2000). The reported toxicities of surfactants vary widely over several orders of magnitude. Consequently, the generalization and extrapolation of such types of data are

difficult to complete. At the same time, anionic and non-ionic surfactant as well as surface-active substance (SAS) builders are relatively non-toxic when compared to various cationic mono-alkyl and di-alkyl quaternary ammonium salts (Scott and Jones 2000). The influence of pesticides and metal ions on surfactant toxicity is hard to predict, although oil-surfactant mixtures are often found to be more toxic than what one would expect. Increases in water hardness and temperature typically lead to higher surfactant toxicity. The fate of all organic pollutants in waste water is determined by several processes including sorption to suspended solids. The adsorption of the cationic and anionic surfactants on carbonates has been investigated by many authors (Ma et al. 2013; Ying 2005).

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The presence of suspended solid particles and naturally occurring dissolved substances decreases the bioavailability of cationic surfactants but not that of anionic and non-ionic ones (Lechuga et al. 2016; Thomas et al. 2009). In the presence of carbonate and silicate suspended particles, the SAS solutions manifest a specific behavior (Cui et al. 2010; Cui et al. 2012; Rosen and Kunjappu 2012; Spataru et al. 2015).

The Nistru River, downstream of Soroca town (Section Varancau), is polluted with pesticides via runoff by storm drains and sewage pipes. The presence of cationic detergents (Sandu et al. 2007; Sandu et al. 2008) can explain the difference between the samples from the Nistru River in Varancau village and the Cunicea village in terms of calcium carbonate impact (Fig. 1). In the sample without the carbonate substrate, nitrification is significant, obtaining high concentrations (12–14 mg/L) of nitrites. Formation of considerable quantities of nitrites shows that from day 11 to day 30 the rate of oxidation of ammonia and the $\text{NO}_3^- \rightarrow \text{NO}_2^-$ reduction exceeds the nitrite ion oxidation $\text{NO}_2^- \rightarrow \text{NO}_3^-$ (Philip et al. 2002; Spataru P 2011). In the sample with calcium carbonate (CaCO_3), the ammonium oxidation is stopped. The nitrite ion concentration is 0.4 mg/L while the nitrate ion concentration remains small in the analyzed sample within the studied period of time. In the same figure, the

dynamics of the concentrations of NH_4^+ and NO_2^- ions for the river in the Cunicea village, whose waters do not contain synthetic surfactants, and the oxidation of ammonia is similar in both samples (with and without CaCO_3).

For the samples taken from downstream Nistru and Prut Rivers, where massive amounts of pesticides from sewage treatment plants reach their waters, this phenomenon is revealed. Wastewaters accumulated in these treatment plants are mostly of domestic origin. In this case, the large amounts of pollutants in wastewaters constitute synthetic detergents. In urban centers, where machine laundering is increasingly practiced, the detergent solubility is not affected by the water hardness. This paper presents a continuation of our research of the water pollution in the Nistru and Prut Rivers with a series of surface-active substances (surfactants, SAS) for small river sections with a different urban influence. The need to investigate the impact of SAS on self-purification and, in particular, on the oxidation of reduced forms of nitrogen in rivers is related to their different influence on the abovementioned processes in river waters. The aim of this paper is to highlight the changes caused by the similar anthropic pollution for several most affected small rivers by this type of pollution adjacent to urban centers in the Republic of Moldova. At the same time, the influence of carbonate suspended particles on the redox processes of water-soluble nitrogen

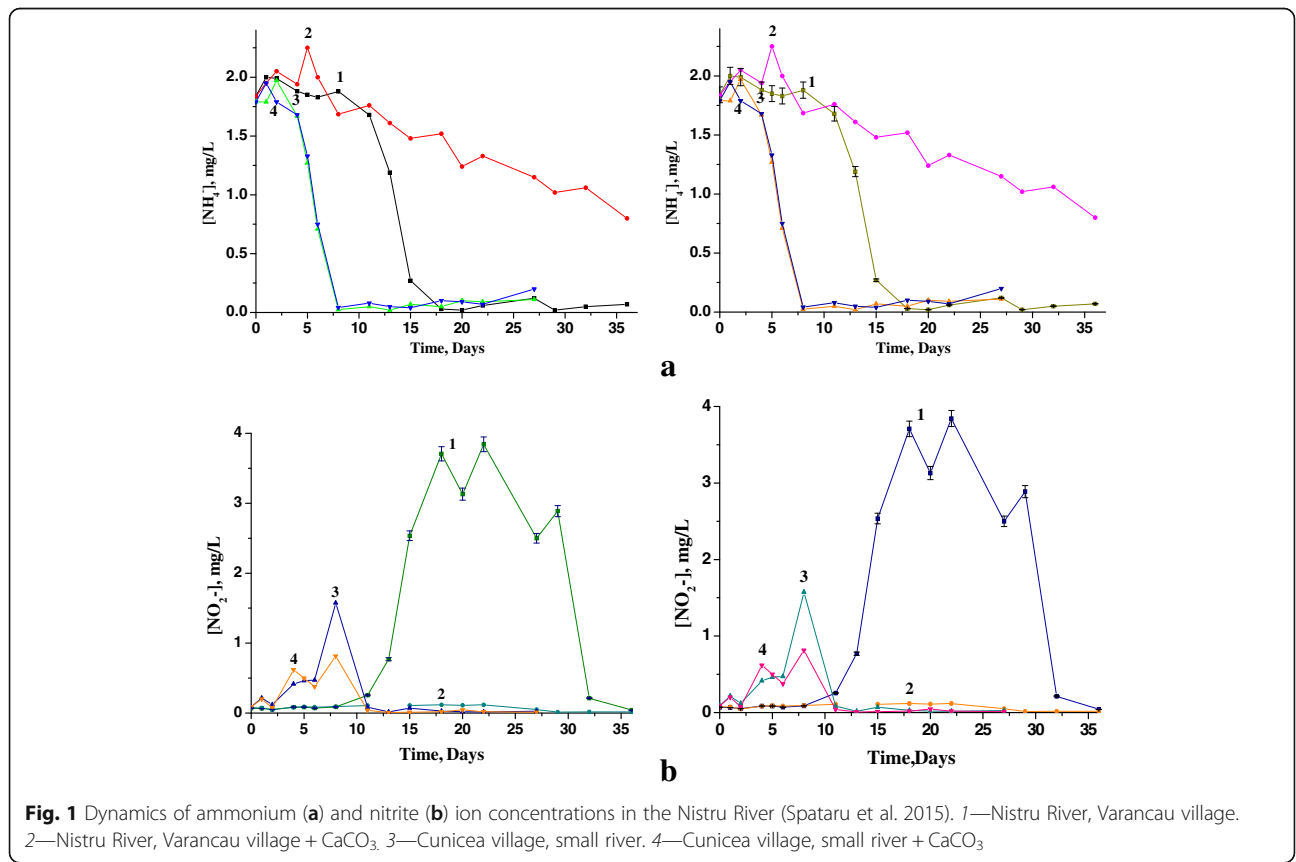


Fig. 1 Dynamics of ammonium (a) and nitrite (b) ion concentrations in the Nistru River (Spataru et al. 2015). 1—Nistru River, Varancau village. 2—Nistru River, Varancau village + CaCO_3 . 3—Cunicea village, small river. 4—Cunicea village, small river + CaCO_3

species has been investigated. Using laboratory simulations, the cationic SAS transfer from the soluble form on the suspended CaCO_3 particles in the presence of an anionic surfactant has been studied.

Methods

A number of water samples were taken from the Isnovat River during October 2015. The tests of natural water were performed according to ISO methods published in specialized literature (ISO 7150–1 2001; ISO 8466–1 1990; SR ISO 7890–3 2000; SM SR EN 26777 2006; Coquery et al. 2005). Laboratory trials were initiated in glass vessels and respected the minimum recommended water-sample model volume (3 L). The same volume and conditions for the whole series of samples from laboratory simulations is essential (Sandu et al. 2014). A solution of $(\text{NH}_4)_2\text{SO}_4$ or NH_4Cl was added to each sample to obtain the ammonium ion concentration between 1.7 and 2.5 mg/L. In the samples, 2 g of chemically pure fine powder of CaCO_3 was added.

The purity of all the used substances corresponded to ISO (ISO 7150–1 2001; ISO 8466–1 1990; SR ISO 7890–3 2000; SM SR EN 26777 2006) requirements. The surface-active substances (lauryl sulfate (LS), cetyltrimethylammonium (CTMA), tetrabutylammonium (TBA)) with at least a purity of 98.5% were used. Water samples from the model were kept in natural lighting and away from direct sunlight. Laboratory simulations were performed under the static conditions. Stirring was performed after each series of tests. The tests were completed at the same time of day. The testing of samples was performed by the UV spectroscopy using Perkin Elmer Lambda 25 and LOMO SFD-46 at the Institute of Chemistry of the Academy of Sciences of Moldova. The contents of ammonium and nitrites in natural water were taken into account in all laboratory simulations.

Results and discussion

Spring samples from the Nistru River and the rivers of the Cunicea village were investigated by means of a model described in Spataru et al. 2015, using water samples both in the presence and absence of CaCO_3 . Braking of the nitrogen oxidation process is known for cationic surfactants and amines (Spataru P 2011). This process has also been studied in the case of the mixture of cationic and anionic detergents. In the presence of anionic surfactants, the toxicity of cationic surfactants decreases (Sandu et al. 2007; Sandu et al. 2008; Spataru P 2011). The changes described in Fig. 2a show that in the presence of CaCO_3 the braking of the ammonium ion oxidation takes place. The standard deviations of the ammonium and nitrite ion test methods are in the ranges of 0.036–0.045 and 0.004–0.027 mg/L, respectively. In the figures showing the dynamics of these

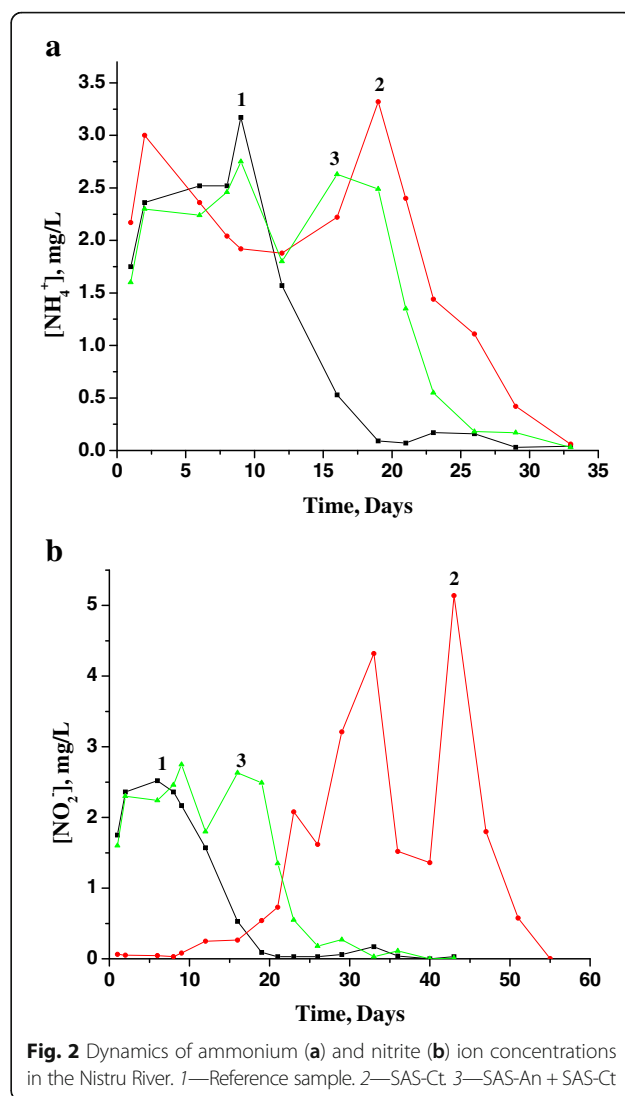


Fig. 2 Dynamics of ammonium (a) and nitrite (b) ion concentrations in the Nistru River. 1—Reference sample. 2—SAS-Ct. 3—SAS-An + SAS-Ct

indices, the error ranges are only indicated at one of the curves, avoiding the picture overload.

The study of dynamic processes in stable soluble forms of nitrogen by laboratory simulations demonstrates diminishing braking effect of nitrification processes in the Nistru River caused, perhaps, by decreasing toxicity in the presence of anionic SAS-Ct (Fig. 2). The cause of this effect may be explained by the fact of the complex [anionic SAS (SAS-An) * cationic SAS (SAS-Ct)] formation. On the contrary, the toxicity of cationic surfactants amplifies with increasing water hardness (Lechuga et al. 2016; Thomas et al. 2009). The phenomenon of the nitrification braking in the presence of CaCO_3 is characteristic for the water in sections downstream of wastewater treatment plants (WWTP) of cities. In the presence of mixtures of cationic and anionic surfactants, the preferential binding of anionic surfactants to calcium carbonate particles has been found (Cui et al.

2010; Cui et al. 2012). Consequently, it can be assumed that the decomposition of the complex of anionic and cationic surfactants contributes to the braking of nitrogen oxidation. Soluble surface-active cationic substances, which have bactericidal effect, remain. Enzyme concentration, which accelerates nitrogen oxidation, decreases. Thus, the CaCO_3 influence can be understood. Additionally, it is expected to suppose the formation of associates of CaCO_3 with anionic organic species, NH_4^+ and NH_2OH , which could also lead to braking of the $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ process (Sandu et al. 2007; Sandu et al. 2008). The decomposition of the complex by treatment with fine powder of CaCO_3 was tested by the UV spectroscopy method.

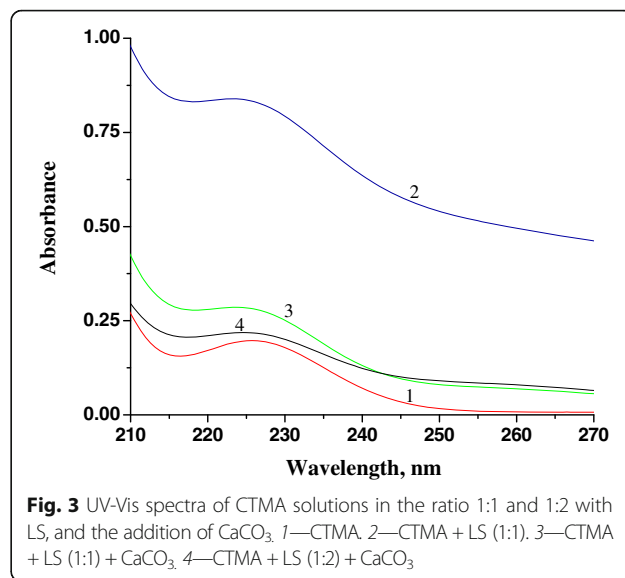
The assessment of these changes was performed using the ability of the complex [SAS-Ct * SAS-An] to have similar but slightly different UV-Vis spectra to that of SAS-Ct. Thus, the complex [CTMA * LS] has a slightly higher spectral line configuration than the 210–250-nm range for CTMA. Using this difference, the change in concentration of this complex can be determined.

Rosen 2004 indicated elsewhere on complex formation between an ionic surfactant and an oppositely charged surfactant of approximately equal hydrophobic chain length with a composition 1:1 (e.g., $\text{C}_{10}\text{H}_{21}\text{N}(\text{CH}_3)_3^+ * \text{C}_{10}\text{H}_{21}\text{SO}_4^-$ or $\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{OH}^+ * \text{C}_{12}\text{H}_{25}\text{SO}_3^-$). Two values of the ratio [CTMA]/[LS] were used in our experiments, 1:1 and 1:2, e.g., corresponding to that of complex stoichiometric composition and to excess of SAS-An. We studied spectra for solutions of CTMA (10^{-5} mol/L) alone and together with LS in the presence of CaCO_3 particles, demonstrating considerable changes among the various aqueous solutions. The spectra movement of complex [CTMA * LS] solution in the absence of CaCO_3 particles and in presence of substrate when compared to that of CTMA solution alone demonstrates almost complete breakdown of the combination [CTMA * LS] caused by the presence of CaCO_3 nanoparticles.

Thus reducing spectrum solution [CTMA * LS] values in the presence of CaCO_3 and their proximity to the spectrum of only CTMA solution proves breakdown of the combination [CTMA * LS] caused by the presence of CaCO_3 nanoparticles. It is necessary to note that in the solution remains SAS-Ct. The change of the combination may be by SAS orientation binding on the particulate carbonate surface, wherein the LS formed a first layer (Cui et al. 2010).

The UV-Vis spectra (Fig. 3) of the same quaternary ammonium (in combination with LS taken in different proportions) solution without and with CaCO_3 particles in their presence proves the impact of lauryl sulfate on the registered changes.

UV-Vis spectra of lauryl, tetrabutylammonium UV solution with and without carbonate nanoparticles show a different behavior, which is not evident in any of the LS

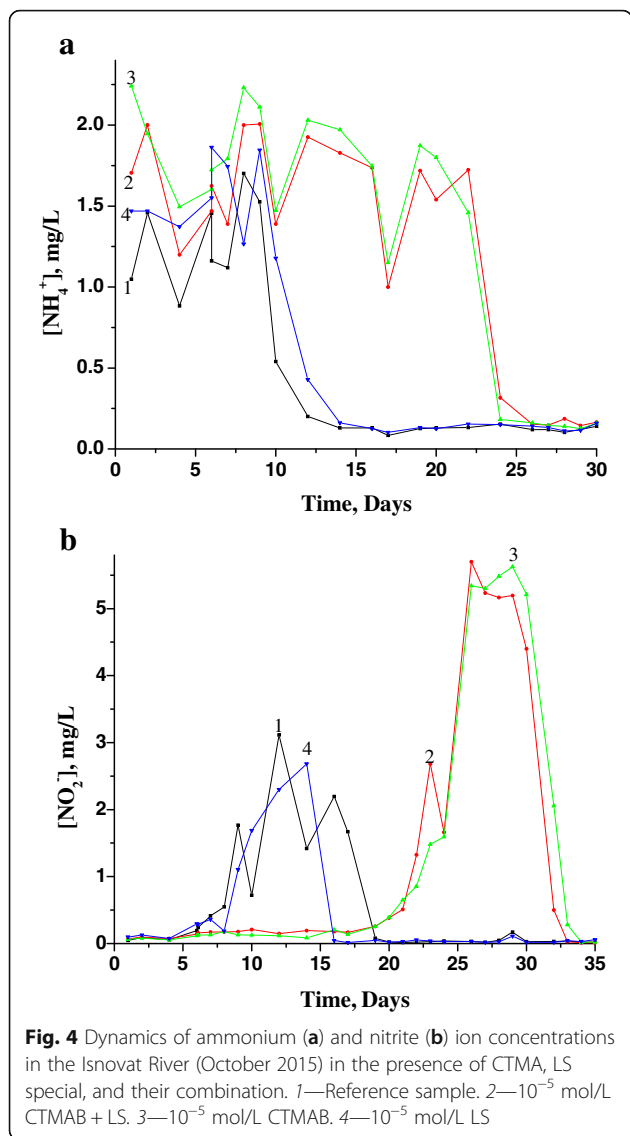


impact or CaCO_3 nanoparticles. Thus, the formation of the SAS-Ct * SAS-An and changes occurring under the impact of calcium carbonate particles is due to geometry, imposed by the mostly hydrophobic chain length of quaternary ammonium species.

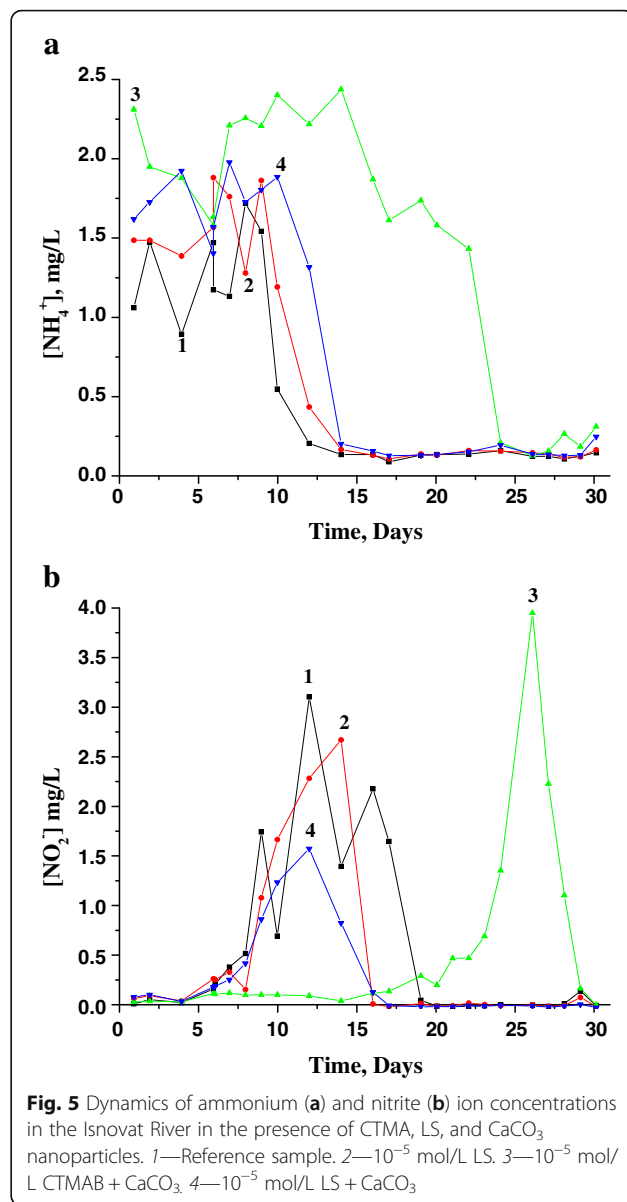
In the simulation laboratory study, a surface change of CaCO_3 particles was highlighted differently on UV-Vis spectra of aqueous solution of CTMA and TBA, with and without NH_4^+ . Both in solutions containing long chain of cetyltrimethylammonium and in those containing tetrabutylammonium with the same dimensions, upon adding ammonium ion (10^2 mg/L), the change of SAS concentration is evident.

UV-Vis spectra of aqueous solutions of only cationic SAS do not show the change in concentration upon addition of fine calcium carbonate particles. Instead, the presence of ammonium ion spectra demonstrates decreasing concentrations of these SAS. Very small effects are observed at 2 mg/L of NH_4^+ ; however, if the concentration of ammonium ions is increased by two orders of magnitude, the effect is marked. Thus, the surface of the calcium carbonate in the absence of ammonium ion selects for SAS-An only; however, upon adding an aqueous solution of NH_4^+ , the surface of the CaCO_3 particles may adsorb both the anionic and the cationic SAS. This effect does not depend on the structure of cationic SAS. One can understand that change occurs at the interface of carbonate particles/solution.

Studying the dynamics of concentrations of ammonium and nitrite ions into the Isnovat River after a massive rain gives the opportunity to conduct complex research. Laboratory simulations include CTMA and LS samples separately as well as added together, and the same samples with suspended particles of CaCO_3 (Figs. 4 and 5). SAS sample (Fig. 4a) oxidation of ammonium ion dynamics



highlights the CTMA and LS impact braking. This is without a contribution to reduce the harmful effects mentioned above. This effect can be caused by various substances on the cationogen sample's active surface until the adding the cationic surfactant provided in laboratory simulations. Thus, LS can be linked to other more stable units with substances reached by washing in water catchment areas. The SAS effect is evident only due to the dynamics of nitrite ions and organic matter, which stimulates the oxidation of nitrite ion comparing with ammonium ion oxidation. Due to the effect of the same SAS, and that of carbonate particles, the dynamics of concentrations of ions NH_4^+ and NO_2^- has a different runway (Fig. 5). In the sample with LS and CaCO_3 , the retardation of oxidation as compared to the reference sample without calcium carbonate particles is evident. In this case we could speak about a braking effect of suspended CaCO_3



particles. This effect is characteristic only for natural waters polluted with organic cationogen substances. It should be noted that carbonaceous particles in suspension reduces formation time and oxidation of nitrite ions. Thus, the peak area of the dynamic NO_2^- is 2–10 times less than in samples with CaCO_3 particles as compared to samples with the same composition except that CaCO_3 particles are missing (Figs. 4b and 5b). Using published research of the persistence of relatively high nitrite ion concentrations (Philip et al. 2002), one could admit two causes that influence NO_2^- dynamics: competition of organic matter in the redox reactions for potential oxidants and substances which are toxic to bacteria generating nitrite-oxidative enzymes.

In the polluted aqueous environment of the Isnovat River, both versions are possible (Thomas et al. 2009; Spataru P 2011). They assume washing farmland producing secondary pollution by pesticides as well as the SAS from wastewater drain into the river.

Bic and Raut Rivers are more affected by an urban phenomenon than Isnovat. Data from the State Hydro-meteorological Service (SHS) is available for mixing river water with water from a wastewater treatment plant (WWTP). In 2013, the Bic River physico-chemical tests showed that maximum allowable concentration (MAC) for the ammonium content exceeded from 40.4 to 78.1 times (in 10 of 12 samples); BOD₅ MAC (in 5 samples) exceeded from 50.3 to 79.67 times, and dissolved oxygen (in 11 samples) was below the fish subsistence level.

In 2014 exceedances of MAC for ammonium were from 40.2 to 84.6 times (in 11 from 12 samples) and MAC for biochemical oxygen demand after 5 days (CBO₅) was exceeded (in 9 samples) from 50.3 to 80.0 times, the dissolved oxygen in 10 samples of water of this river was below the subsistence fish. Braking self-purification/nitrification processes occur over several tens of kilometers to the confluence with the Nistru River. Table 1 shows some of the quality indicators that prove the deplorable state of the Bic River water. The Bic River situation starts from unpurified water shedding from WWTP of Chisinau into it and their impact on the Nistru River. Mixing of the Bic water with the Nistru one devolves on a more larger portion of the river than 200 m. However, the large impact of these pollutants and pesticides is marked.

Bic River water downstream of the treatment plant contains large amounts of organic matter (chemical oxygen demand (COD) = 433–480 mg/L). After shedding of water passed through the technology WWTP of Chisinau in Bic (Table 1) and derived from channeling the city's predominantly domestic wastewater (from residential apartments), one could assume that the population of bacteria specific to this medium has developed to the estuary inhabited of the Bic River in the Nistru River. The large concentration

Table 1 Indicators of water quality of the Nistru and Bic Rivers at their confluence

Indic./sample	Nistru River, upstream to the confluence of the Bic River	Bic River, upstream to the confluence of the Nistru River	Nistru River, 200 m downstream of the confluence with the Bic River
pH	8.18	7.62	7.71
[NH ₄ ⁺], mg/L	0.257	51.0	42.3
[NO ₂ ⁻], mg/L	0.156	0.253	0.242
[NO ₃ ⁻], mg/L	5.6	0	0
Oxygen, mgO/L	8.71	0	0
CBO ₅ , mgO/L	0.67	97.8	93.4
CCO _{Cr} , mgO/L	17.0	150	144

of organic substances (most of which being easily degradable) will cause further reduction of dissolved in water nitrogen to its reduced form, ammonia. Ratio CBO₅/COD confirms clearly that about 65% of organic substances in water are easily degradable biochemically in the section of the Bic River confluence with the Nistru River (Table 1). The cationic organic and organic halogen compounds (with impact braking processes of nitrification/self cleaning) have relatively low organic matter river water. Therefore, the related associations with other species of the organic component may cause a toxic effect more pronounced only after a period of time in which a large consumption of the naturally organic matter occurs. Thus, it is logical that the braking effect is stronger in nitrite dynamic changes which occur after a certain time. That is why in samples of polluted water from the Bic and Nistru Rivers (diluted with the Nistru River water) relatively high

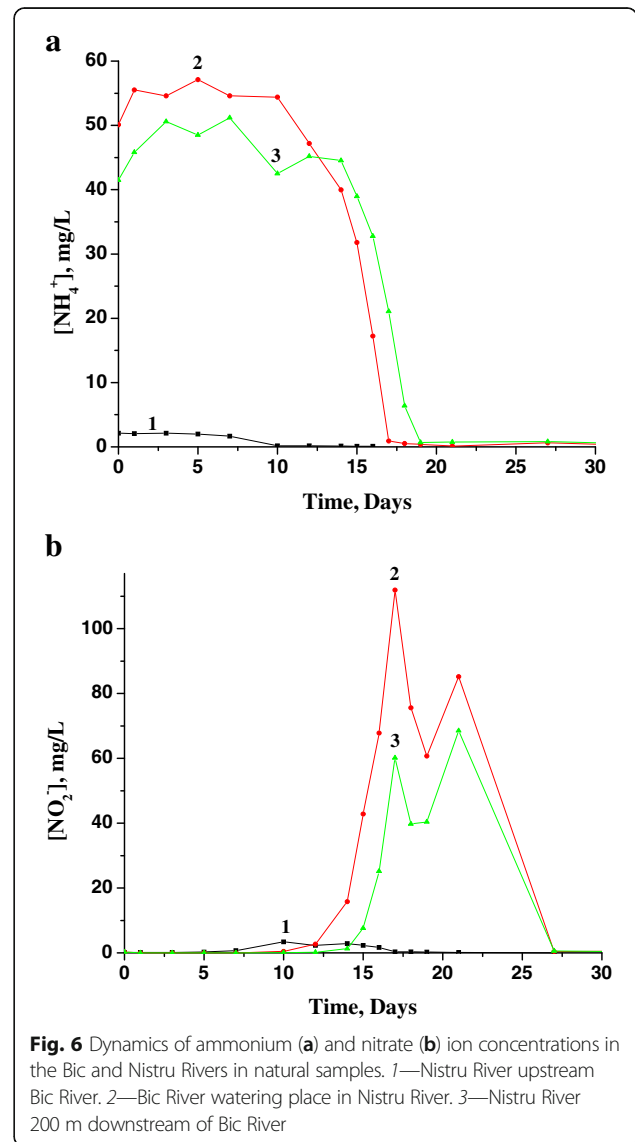


Fig. 6 Dynamics of ammonium (a) and nitrate (b) ion concentrations in the Bic and Nistru Rivers in natural samples. 1—Nistru River upstream Bic River. 2—Bic River watering place in Nistru River. 3—Nistru River 200 m downstream of Bic River

concentrations persist longer than for nitrite water samples from the river. In ammonium ion dynamics, this difference does not exist (Fig. 6).

Operation below the required standards of WWTP Balti has the same cause. From our data, the most obvious and serious pollution occurs upstream and downstream of the Balti city, causing great concern for high ammonia content in the Raut River water downstream of Balti. There are multiple cases of upper limit of average concentrations of 7.03 mgN/L (18.02 MAC) and the maximum value detected being 22.3 mgN/L (57.18 MAC). These maximum concentrations are recorded during the spring and summer, when juvenile fish development is very sensitive even to low concentrations of ammonia. This impact in WWTP activity is caused by changing the composition of organic matter and especially in the increasingly significant SAS-Ct.

Conclusions

Dynamics of ammonium and nitrite ion concentrations in the Isnovat River highlights braking nitrification/self cleaning of the water samples containing a cationic surfactant as CTMA. The influence of CaCO₃ on the toxicity and SAS interaction with different long chain (hydrophobic) groups of organic radicals and electrostatic groups is obvious. UV-Vis spectra exhibit the interaction described above, which leads to a reduction of STA in the solution. Experiences have proved the changes in the SAS interaction with CaCO₃ particles, depending on the proportions of these substances in water. The higher the concentration ratio of SAS-An in aqueous solution (LS) compared to that in the cationic, the separation of the latter occurs completely. So, the transfer and the reorientation of CTMA to carbonate particles takes place depending on the amount of LS. So, the decomposition occurs in combining CTMA * LS and depositing them on nanoparticles, wherein the first bonding layer is formed with LS, and the rest are oriented based on the hydrophobic chain and group electrostatic interaction. This effect of shift results in a change of environmental toxicity. Both UV-Vis spectra and laboratory simulations establish the change due to the addition of calcium carbonate. Simulations and laboratory tests of water samples from Isnovat, Bic, and Raut Rivers demonstrate the SAS-Ct has a significant influence on treatment and self-purification processes.

Abbreviations

CaCO₃: Calcium carbonate; CBO₅: Biochemical oxygen demand after 5 days; COD: Chemical oxygen demand; CTMA: Cetyltrimethylammonium; LS: Lauryl sulfate; MAC: Maximum allowable concentration; SAS: Surface-active substances (surfactants); SAS-An: Anionic SAS; SAS-Ct: Cationic SAS; TBA: Tetrabutylammonium; WWTP: Wastewater treatment plant

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Authors' contributions

PS developed the concept and carried out the field data collection and data analysis. PS, TS, and IP drafted the manuscript. FF, JWS, and OS made comments on the manuscript. All authors read revised and approved the manuscript.

Competing interests

The authors declare that they have no competing interests.

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