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RISK TO HUMAN HEALTH CAUSED BY NON CONDITIONAL DRINKING WATER

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Abstract: *Drinking water quality is one of the key factors that may cause harmful effects to health, especially during lasting continuous consumption. This report analyzes information on current state of some basic health factors for Chernivtsi citizens depending on their place of living and consuming drinking water from local wells. Non quality contact medium risk analysis and some peculiarities of this function application for problem of kinetic modelling are under discussion as well. The analysis of risk increase effects during natural nitrification process on the basis of two kinetic models of the nitrification cycle is studied. The analysis is focused on two cases: when enzymes concentrations are constant and when nitrifying bacteria grow. The numerical solution of kinetic model and geo-informatical analysis are used to explain possible causes of high risk values and oncological diseases occurrences that may be caused by nitrate contamination. The question: why nitrates pollution level correlates with oncological pathology is under discussion of the study. An attempt to forecast health quality factors for citizens taking into consideration nitrogen intermediates is made. A simple kinetic model of immune status of people under chemical pollution of drinking water is considered as well. A comparison of the results of simulation with real statistic illnesses data and contaminant dispersion is the subject of the study.*

Keywords: *drinking water quality, risk assessment, mathematical model, illnesses, nitrite, nitrate, kinetic, nitrification cycle.*

1. Introduction

Health risk assessment is one of the elements for methodology of risk analysis that pre-empts risk assessment, determines risk and informs about risk factors. From the point of view of science health risk assessment is a successive, systemic consideration of all the aspects of a factor or factors' influence being analysed on human health including admissible levels of influence. Most typically in practice while making risk assessment is obtaining and generalizing data about possible influence of human environment factors on health necessary and sufficient for hygienic argumentation of optimized, substantiated managerial decisions to eliminate, decrease or taking pre-emptive actions against environmental pollution, environmental objects monitoring optimization [1]. Among typical practical tasks is to work out methods and strategy of regulation measures, by comparing and ranking degrees of manifestation of human environment influence factors, formulation and adoption of more reliable and safer levels of influence and hygienic standards, monitoring direct and indirect indicators of human health and health risks. Thus, in such a way it is possible to improve the system of hygienic regulation and its harmonization with internationally established principles, criteria and methods of establishing safe levels of chemical substances influencing human health.

2. Materials and methods

Modern methodology for comparative risk assessment for human health is based on risk factors connected with contact environments. As a rule, comparative assessment precedes conducting in-depth studies of risk assessment and is done on the basis of the data about possible adverse effects of chemical substances. On the previous stage it is useful to apply a conceptual model of the area that is an aggregate of ties between the objects of the system under study.

The objective of the present paper is to make an attempt to calculate risk factors, draw a comparison of computational methodologies and provide explanation of the influence on health based on example of using surface waters of poor quality for consumption needs by population. And to explain possible reasons of correlation of cancer disease rate with the level of nitrate pollution.

In a previous paper (Skip and Nakonechny, 2010, In press) a poor correlation between the quality of drinking water of decentralized water supply (nitrate contents) and cancer sickness rate, in particular general pathology, and that of digestive apparatus and abdominal cavity localized similarly to distribution of surface waters contamination by nitrates is made. The area under study is characterized by the absence of industrial companies and other overland runoffs except those of private households. That is why the number of toxic substances in water is limited to health protection unit, decree #383 “drinking water” [2] with a list of substances to be under control that are monitored. Among these substances we can single out typical ones among carcinogens [3-5] according to their maximum admissible concentration (MAC) in ground water (e.g. some pesticides, surfactants) or known and probable human carcinogens [6] (ammonium, nitrates, nitrites). It is worth mentioning that some pesticides such as DDT have not been used for at least ten years, and according to water samples from wells these substances are not found. That is why to establish the area distribution according to this pollutant is not possible. Thus, the main factors of carcinogenic risk are nitrogen-containing compounds in concentrations that get closer to or exceed their MAC and also new synthetic organic substances (surfactants, pesticides) that are not included in the list that regulates drinking water in Ukraine. But such an analysis of the situation needs detailed chemical analysis of organic substances in drinking water. Due to the lack of technical and financial possibility to carry out such studies their analysis is beyond the objective of the present paper.

That is why we shall dwell on the previous methodology of nitrate pollution. The well known nitrification chain of ammonia nitrogen with enzyme catalysis can be described by the following reactions:

$$NH_4^+ + E_1 \underset{k_{01}}{\overset{k_1}{\rightleftarrows}} [E_1NH_4^+] \qquad (1)$$

$$[E_1NH_4^+] + 3/2O_2 \xrightarrow{k_2} NO_2^- + 2H^+ + 1/2H_2O + E_1 \qquad (2)$$

$$NO_2^- + E_2 \underset{k_{03}}{\overset{k_3}{\rightleftarrows}} [E_2NO_2^-] \qquad (3)$$

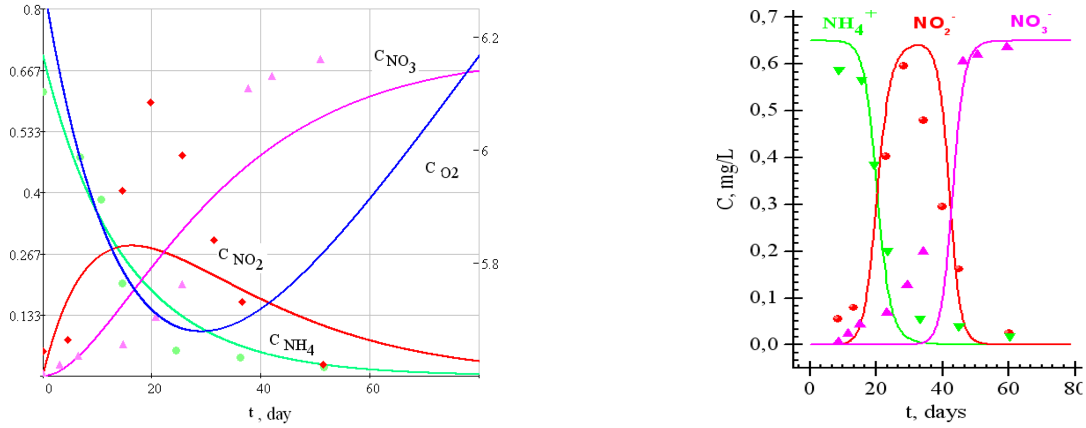
$$[E_2NO_2^-] + 1/2O_2 \xrightarrow{k_4} NO_3^- + E_2 \qquad (4)$$

where E_1, E_2, $[E_1NH_4^+]$, $[E_2NO_2^-]$ – enzymes and corresponding enzyme-substrate compounds. In ground waters after discharge of ammonium nitrogen under favourable conditions and in the presence of nitrifying bacteria, nitrification reactions take place. Model eq. (1)–(4) is the simplest one that accounts for fermentation kinetics.

It does not take into account the reproduction of nitrifying bacteria. As model calibration (establishing constants of appropriate reactions speeds for the process eq.(1)–(4) we used experimental data [7]. The nitrifying bacteria reproduction can be calculated by the Malthus equation as for ground waters substrate contents for nitrification is relatively low, intra-specific competition of the bacteria can be ignored.

As regards the most adequate description of bacteria reproduction kinetics, we can presume in a separate study that the rate of bacteria reproduction will depend on substrate concentration.

As a rule, massive discharge of ammonia nitrogen of faecal origin happens during thawing snow, heavy precipitation, and filtration of waste water from settlers and septic tanks [8]. That is why such a process will be of periodic, stochastic character and, as a result, risk assessment is problematic in terms of current exposition and dose as a function dependent on time and concentration averaging function.



a) **b)**

Figure 1. Nitrification kinetics. Solid lines — model results of concentration, dots and markers – experimental data. (a) without and (b) taking into account nitrifying bacteria reproduction

3. Results and discussion

For risk assessment [1] and different ways of averaging concentration and the rate of polluted water penetration into the body during nitrification, a mathematical model of fermentative process eq.(1) – (4) was used, the results of modelling being shown in Fig. 1 (solid lines). By comparing the field data and modelling results, we can see that the model, taking into account Monod kinetics, satisfactorily describes the dynamics of nitrification.

From the analysing field data [7], (markers in Fig. 1) we can see that nitrification process lasts roughly about fifty days. We can see in Fig. 1 that the secondary contamination in practice requires quite a long time and nitrite ions are found whether nitrate contamination is of a permanent nature.

Comparing MAC values for three forms of nitrogen $MAC_{NH_4^+} = 0.5$, $MAC_{NO_2^-} = 0.1$, $MAC_{NO_3^-} = 50\,mg/l$ (Directive 80/778/ EU [9]), we can see that the most toxic are nitrites and ammonia ions. When calculating MAC values for the above mentioned elements we used reference values. As we can see from Fig. 2a, excess of MAC for ammonia ions and nitrates (as a result of its presence in consumed media) within time framing up to 5 days from the emergence of ammonia nitrogen according to kinetic Fig. 1 – is quite high.

The aggregate pollution on higher levels than MAC 1 is determined by nitrite and ammonia ions and lasts for fifty five days. As nitrification is accompanied by the process of reproduction of the appropriate bacteria from which enzyme concentration depends in water, the components of nitrification process safety assessment will be more accurate taking into account the process of nitrifying bacteria reproduction.

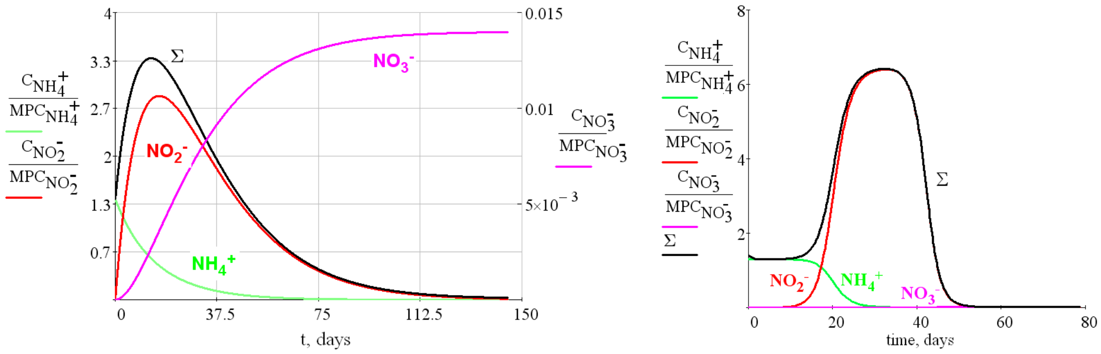
As it turned out from the analysis of modelling outcome, this process is sensitive to the influence of nitrifying bacteria depending on speed of behaviour and duration of secondary (nitrite) pollution. This sensitivity is manifested especially in the decrease of time of massive secondary water pollution (Fig.1b) as a result of Nitrobacter and Nitrosonomas in comparison with the model (Fig. 1a).

Actually the population of these micro organisms is responsible for widely known fact of self-purification of water objects from nitrites and its speed. The presence of toxic components in water and their considerable influence on the body takes (according to nitrites) ≈ 55 days according to the model data and ≈ 50 days according to the experimental data, and health effects in this period of time are substantial.

It is worth mentioning that surpass of MAC (Fig. 1b) of NO_3^- for model situation is not observed (0.014 MAC), and of NO_2^- and NH_4^+ in accordance with model outcome, is 2.8 and 1.4 MAC respectively or in correlation

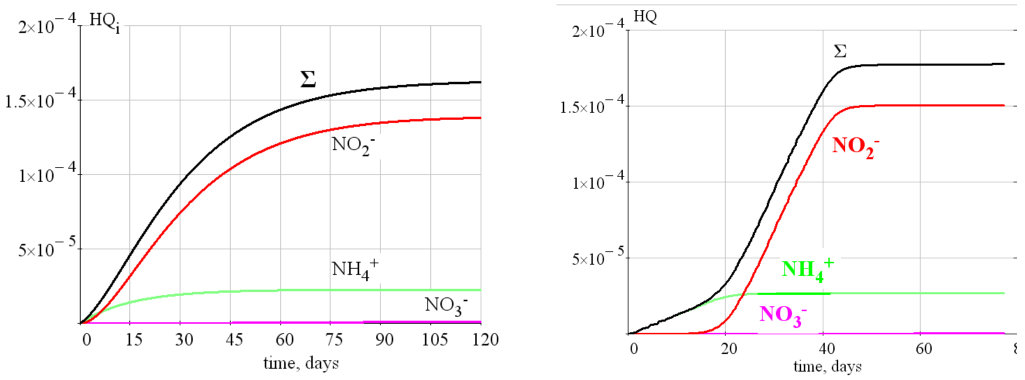
$$\frac{C_{NO_3^-}}{MPC_{NO_3^-}} : \frac{C_{NO_2^-}}{MPC_{NO_2^-}} : \frac{C_{NH_4^+}}{MPC_{NH_4^+}} = 1:200:100$$

It is worth mentioning that MAC



a) b)

Figure 2. Water pollution level. (a) without and (b) taking into account nitrifying bacteria reproduction



a) b)

Figure 3. Pollution substance hazard quotient while consuming water with dynamic concentration of nitrogen forms that contaminate water according to model (1)-(4). Averaging intake of pollutant substance to digestive tract is one day. Intake rate IR(t) = const. (a) without taking into account bacteria reproduction, and (b) taking into account bacteria reproduction.

exceeding (Fig. 2b) for NO_3^- for model situation is not observed (Table 1 line 5), components of nitrification process concentration at the point of time corresponding to the maximum of nitrites have the correlation

$NO_3^-: NH_4^+: NO_2^- = 1:467:2.1\cdot10^5$.

As we can see by comparing Fig. 1a and 1b, taking into account nitrifying bacteria reproduction, it describes ammonia nitrogen transition to nitrate more realistically in the nitrification model. Major water pollution will be caused by aggregate ammonia and nitrite contamination at the level of 6.4 of the part of MAC. The level of pollution will be at the limit of designation that is a negligibly small value. But hazard quotient calculated by using the average of concentration will be incorrect for the model after fifty day-time (Fig. 3b), as after 50 days neither ammonia nor nitrite nitrogen in water in essential concentrations will be observed (Fig. 1b and 2b). By applying equations (5) and (6) we can see that concentration changes in time and hazard quotient has different form in time frame up to 50 days. But taking into account the concentration changes of all the forms of nitrogen during nitrification enables us to calculate more accurately the hazard quotient.

Such an approach to hazard quotient in practice is somewhat inconvenient: first, it is next to impossible in most cases to establish the onset of ammonia ions getting into ground water. Taking into account the change in concentration in time implies constant monitoring of water object that is possible only in automatic stations. In most cases specific hazard quotients are calculated for averaging concentrations as discrete quantities but for complex integral assessment of hazard quotient and use of risk function for modelling pollution impact on population health consuming such coupling medium, a continuous function is needed.

According to [1] health risk may be assessed by consumed dose as:

$$Dose = \int_{t_1}^{t_2} C(t)\cdot IR(t)dt\,, \qquad (5)$$

$C(t)$ – concentration and $IR(t)$ – intake rate of intake of contaminant substance during time t_2–t_1.or:

$$Dose = \frac{C\cdot V\cdot EF\cdot ED}{W\cdot AT\cdot 365}, \qquad (6)$$

under conditions $C(t)$ and $IR(t)$ = const. ED= t_2–t_1, V – volume of consumed medium (water), EF – rate of event of consumption, W – weight, AT – exposition time extrapolation. Taking into account the substance toxicity that is determined by its MAC or reference dose then hazard quotient may be calculated:

$$HQ=Dose/RfD. \qquad (7)$$

The analysis of correlation (6) and Fig. 3 indicate constant increase of consumed nitrates dose and absence of dose decrease with the absence or decrease of pollution level for nitrites and ammonia after fifty days from the onset of nitrification process.

Without taking into account the nitrate

Table 1

Correlation of inorganic nitrogen forms during nitrification process

№	$C_{NH_4^+}/MPC_{NH_4^+}$	$C_{NO_2^-}/MPC_{NO_2^-}$	$C_{NO_3^-}/MPC_{C_{NO_3^-}}$	Σ
1	0.4	1	0.0025	1
2	0.5	5.9	0.0016	6.4
3	0.15	0.84	0.004	1
4	0.87	5.6	$9\cdot10^{-3}$	6.4
5	0.014	6.4	$3\cdot10^{-5}$	6.4
6	0.35	6	0.004	6.3

Lines No. 1,2 – stoichiometric calculations.
Lines No. 3,4 – model data without taking into account bacteria reproduction.
Lines No. 5 – model data when taking into account bacteria reproduction.
Lines No. 6 – experimental data [7].

consumption by biota, the dependency of hazard quotient of each of the nitrification process components on time, shown in Fig. 3, is depicted by bold curves. By analysing the data received, it turned out that ammonia nitrogen hazard quotient increases steadily in time. Nitrite and nitrate forms of nitrogen have similar tendencies that unlike the dynamics of concentrations Fig. 1, are of monotonous increasing nature. The hazard quotient values of ammonia ions and nitrites do not exceed the values of $2.3\cdot10^{-5}$ and $1.4\cdot10^{-4}$ respectively. The hazard quotient caused by nitrites which value is $1.3\cdot10^{-6}$ is considerably lower than ammonia and nitrite hazard quotients. Thus, the risk caused by NO_3^- is considerably insignificant compared with NH_4^+ and NO_2^- risks. As in real practical activity in Ukraine the quality control of decentralised water supply is made for NO_3^- concentration, then NO_2^- and NH_4^+ concentration may reach dangerous, including carcinogenic nature, values; as a result correlation of most conservative component of nitrification process NO_3^- , there is a cancer rate observed in practice (Skip and Nakonechny, 2010. In press.). Aggregate hazard quotient may be calculated for the situation with ground water contamination by household nitrogen containing discharges, e.g. for a situation mentioned in (Skip and Nakonechny, 2010. In press.).

A weak correlation between high content of nitrates and oncological pathology is observed. But nitrates at present do not belong to carcinogens or potential carcinogenic substances. That is why oncological pathology may be caused by nitrite ions causing secondary water contamination in the nitrification process. There is a logical question: how do ion NO_3^- concentrations correspond to ions NH_4^+ and NO_2^- concentration values on similar or lower than MAC levels? To answer the question we shall use the procedure of minimization for calculating these values.

In this way we obtained the correlation of concentrations (Table 1 line 2) that corresponded to lower or equal MAC values for three forms of nitrogen at the moment of maximum nitrite concentration.

It follows that out of the three forms of nitrogen during natural nitrification process, decisive contribution to toxic and possibly carcinogenic risks will be caused by intermediate form of nitrogen – nitrites, and toxic – by a combination of ammonia and nitrite ions, and toxic risk – by ammonia ions and nitrites. Though in literature [10, 11] there is no clear view about cancerogenity of nitrates and nitrites on human body, from the point of view of chemistry, nitrosation reaction in a human body is possible. And thus nitrosation products – nitrosamine are carcinogenic. Moreover, transferring the experiments' results on animals is not always adequate for the effects observed in a human being. That is why the information about the absence of carcinogenic effect in lab mice, rats etc. may not coincide with epidemiological studies for the inhabitants of the locality in question. In such cases it is obviously necessary to use the results of statistical observations of the ground water pollution level and epidemiological data as most reliable source of information about the influence of separate substances on the disease rate. Of course, in practice in ground water there is a great number of organic, including nitrogen-containing substances. But having a systemic monitoring of sources of water supply in terms of quantitative and qualitative analyses of contamination and applying modern multivariate analysis or neural networks one can with sufficient reliability establish the cause and effects of the relationship dose-effect as such, and effects of synergism.

It is worth mentioning that consumed dose calculation is sensitive to time of averaging concentration of polluting substances. If the time of averaging concentration, e.g. takes up 146 days (maximum model time), then for contamination that took place about thirty days, the averaging will lead to the case when toxic effect (exceeding the average concentration of 1 MAC) will not be observed.

Alternative way of pollution level assessment may be made using stoichiometric nitrification reaction. As can be seen from figure (1)–(3), 1 mol of nitrate ions is formed by 1 mol of nitrite ions and 1 mol of ammonia ions. If the water pollution level of nitrates reaches 9 MAC, e.g. for ground water (B.Skip and K.Nakonechny, 2010, In press.), then it will be $\nu_{NO_3^-} = \frac{9 \cdot MAC_{NO_3^-} \cdot 10^{-3}}{Mr_{NO_3^-}}$ mol (the hypothesis is that we have 1 liter of water in natural setting). This number of nitrates formed from an equivalent quantity of nitrites, and exceeding water pollution in ammonia will make $\frac{\nu_{NO_3^-} \cdot Mr_{NH_4^+}}{MAC_{NH_4^+} \cdot 10^{-3}} = 261.3$ and nitrites $\frac{\nu_{NO_3^-} \cdot Mr_{NO_2^-}}{MAC_{NO_3^-} \cdot 10^{-3}} = 3338$ times. The approximate water toxicity may be assessed as 4.8% and 0.2% for values LD_{50} respectively for nitrites and ammonia ions for a grown-up.

When nitrate pollution level is 1 MAC, the concentration of ammonia and nitrate forms will be 29 and 371 MAC respectively. Thus, the controlling of pollution level of drinking water only by nitrate level according to health protection unit, decree #383 “drinking water” [2] or Directive 80/778/EEC [9] does not require conformity to standard. But such an approach in health protection unit, decree #383 “drinking water” [2] to drinking water quality assessment of decentralized water supply causes dangerous situation in terms of health risks, including carcinogenic ones. Apparently while assessing safety of drinking water consumption we should depart from allowable levels of water pollution by nitrites and ammonia ions. The calculations show that the water pollution level during nitrification process with interconnected nitrogen forms has the values from Table 1 line 1.

But we have to mention that stoichiometric calculations do not allow for length of nitrification process and dilution by ground waters. That is why at any moment components of nitrification reaction concentration will be lower and calculated by nitrification kinetics and process variances in aquifer. Exceeding admissible level of drinking water contamination by inorganic nitrogen forms value $C_{NO_3^-} / MPC_{C_{NO_3^-}}$ or increase over the period of time less than fifty-five days larger than 0.004 that demonstrates exceeding admissible pollution level of drinking water by nitrites or ammonia in the past (according to model data) in areas of aquifer that is adjacent to pollution sources, should be avoided.

Referring back to experimental values of nitrates concentrations in wells, we can see that there are areas where the correlations of nitrate content and oncological disease rate exceed 9 MAC. Thus, water pollution level of ammonia ions and nitrites had to exceed permissible level of 261 and 3338 times respectively.

Insignificant discrepancy of values received by stoichiometric calculations (Table 1 line 2) and kinetic model (Table 1 lines 4 and 5) is evidently stipulated by not taking into account the dispersion of substances in aquifer, nitrification kinetics, kinetics of nitrifying bacteria reproduction, and difficulty to keep to the purity of experiment in real ecosystem with a great number of sources and asynchronous inflow of nitrogen-containing substances. This is corroborated by insignificantly understated outcomes between model values of nitrites concentrations with experimental ones, Fig. 1, and similar concentrations [7] ammonia and nitrite ions concentrations. The most probable reason of such discrepancy is a repeated inflow of ammonia ions. But despite the above mentioned drawbacks, the values of relative concentrations of nitrate ions in water may be used as an indicator of the water pollution level during nitrification process in aquifer by ammonia ions and nitrites. For sources of decentralized water supply from ground water, it is necessary to ensure in appropriate regulatory documents to make tests on the availability of nitrites and ammonia ions in water samples as mandatory with a frequency not exceeding half of massive nitrite pollution duration ~25 days to discover real state of affairs by nitrite and ammonia water pollutions and to prevent possible oncological effects.

4. Conclusions

Therefore while establishing standard values for ammonia and nitrite nitrogen forms it is necessary to comply with the calculated values (Table 1). The simplest is the stoichiometric calculation. Otherwise, the risk of oncological diseases onset will remain at a significant level and toxic poisoning by nitrites and ammonia ions is possible. As NH_4^+ and NO_3^- do not belong to apparent carcinogens, but nitrification process indirectly causes carcinogenic effect by means of secondary pollution by nitrites, that is why it is reasonable to consider ammonia ions as potential carcinogens or substances that potentially cause carcinogens formation for ground water and ground water supply. Another alternative possibility is to consider carcinogens nitrification process with the above mentioned MAC.

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