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Drinking Water Engineering and Science Discussions

Interactive comment on "Conversion of organic micropollutants with limited bromate formation during the Peroxone process in drinking water treatment" *by* A. H. Knol et al.

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Anonymous Referee #2

Thank you very much for your compliments and remarks. The paper will certainly benefit from your comments. Point by point we will respond to your remarks. The changes in the manuscript are marked with R2.

General comments

The abstract is written in the present tense, where the past tense is more appropriatie. The authors agree and the tense is changed.

In the abstract, the results and discussion and the conclusions chapters it is stated that “the peroxone process can be controlled on basis of temperature, bicarbonate and TOC”. However, from the text it is not clear how this can be done. On page 24 (line 9) it is mentioned that NOM influences ozone consumption, then on page 25 (line 5) it is said that DOC is not relevant for bromate formation and in the conclusions it is concluded that peroxone can be controlled by measuring DOC. Please explain better. The authors agree that it can be explained better. We changed p 15, line 7 - 22: “As expected, the conversion of the model compounds – with the exception of metformin which was hardly converted at all – increased with increasing water temperature and decreasing concentrations of DOC and bicarbonate. The concentrations of bicarbonate and DOC and the water temperature fluctuate seasonally (Fig. 7. All three parameters could be (partly) responsible for the varying conversion of the five model compounds), for sure these three parameters strengthen each other. However, as we did not have test conditions in which only one of the parameters could be varied, it is not possible to distinguish causation and co-correlation. The fact that bromate formation and OMP conversion appears to be dependent on water temperature, bicarbonate and/or DOC concentration has as practical implication that in summer seasons the ozone dose strictly needs to be limited to 1.5mgL-1 whereas in winter season a higher ozone dose is allowed to achieve the optimum OMP conversion with acceptable bromate formation. In this way the bromate formation and the conversion of OMPs are levelled over the year. Controlling peroxone on basis of the (derived) parameters water temperature, bicarbonate and DOC and monitoring of bromate formation is feasible.” In: “The conversion of OMPs increased with increasing water temperature and decreasing concentrations of DOC and bicarbonate. The bromate formation increased with increasing water temperature and bicarbonate concentration. Furthermore, the conversion of OMPs and bromate formation increased with ozone dose and the bromate formation was reduced by increasing the dose of hydrogen peroxide. Therefore, the conversion of OMPs and bromate formation can be levelled by adjusting the ozone and hydrogen peroxide doses to water temperature, DOC and bicarbonate: In winter

DWESD
8, C41–C48, 2015

period the conversion of OMPs can be increased by increasing the ozone dose without exceeding the target bromate value and in summer period the bromate formation can be reduced by increasing the hydrogen peroxide dose, without effect on the conversion of OMPs. Controlling peroxone on basis of the online measured or derived parameters as water temperature, bicarbonate and DOC is feasible."

In the abstract and the introduction to the "strict Dutch guideline", while the limit of 0.5 _g/L of bromate is more a target. Do not refer to company standards. The authors agree: "Company standard" is removed in the text. We changed on p 2, line 11: "the strict Dutch guideline for bromate in drinking water" In: "the strict Dutch drinking water act for bromate of 1 μgL-1" We added on p 4, line 26: "The target value of this research was an average bromate formation of 0.5 ugL-1 with a maximum of 1 ugL-1."

Duplications and superfluous information have to be avoided in the text. The authors agree and accepted the remarks from the Anonymous Referee #2 hereafter.

Start conclusions chapter with a small introduction of the purpose of the paper. The authors added on p 15, line 24: "Advanced oxidation with O3/H2O2 was conducted on pilot plant scale on pre-treated Meuse river water to investigate the conversion of 14 selected organic micropollutants and the formation of bromate. "

Specific comments: Pg 22, Line 8-9: sentence needs rephrasing: The authors changed: "The conversion of OMPs can be increased by further increasing the ozone dose, however, the ozone dose is limited concerning the bromate formation." In: "The ozone dose was the main factor in the conversion of the model compounds, however, the ozone dose was limited because of bromate formation."

Pg 22, Line 11-12 sentence needs rephrasing The authors changed: "In terms of limited chemical consumption, maximal conversion and adherence to the strict Dutch guideline for bromate in drinking water, a practical full-scale setting is 6 mgL-1 hydrogen peroxide and 1.5 mgL-1 ozone." In: "In terms of limited chemical consumption, maximal conversion and to comply the strict Dutch drinking water act for bromate of

DWESD
8, C41–C48, 2015

1 μgL-1, a practical peroxone setting was 6 mgL-1 hydrogen peroxide and 1.5 mgL-1 ozone."

Pg22, line 18-10: delete "below : : : formed" (not needed) Pg 23, line 2: insert "all" before OMP Pg 23, line 4, delete "more" Pg 23, line 8, 9 and 10: delete "at the moment", "fully to" and "Mainly the" respectively. The authors agree and changes are made according proposals.

Pg23, line 12-13 needs rephrasing The authors changed: "Polar OMPs are less well adsorbed and/or converted (IJpelaar, 2008)." In: "Polar OMPs are adsorbed less and/or converted (IJpelaar, 2008)."

Pg 23, line 13-16: delete "OMPS with: : :. for customer perception" Pg 23, line 16-17: swap "detected" and "structurally" Pg 23, line 18: delete "at present" Pg 23, line 22: insert "the" before "most" Pg 23, line 23: "these" = "this" Pg 23, line 24: "this" = "these" Pg 23, line 27: delete "very" Pg 23, line 28-Pg 24, line 25: text suggestion" Although the reaction rate of direct oxidation, depending on the type of compounds, is relatively: : :..(Gottschalk et al., 2010), and the reaction rate: : :: : :..1010 M-1s-1, direct oxidation cannot be neglected when applying peroxone. The authors agree and changes are made according proposals.

Pg 24 line 1: explain to which equation the kinetics parameter k belongs. We changed p 3, line 28 – 29: "The reaction rate of direct oxidation depends on the type of compounds," In: "The reaction rate of ozone depends on the type of compounds,"

Pg 24 line 16: delete the sentence "There is also: : : 2 _g/L." Pg 24, line 20: delete "in the Netherlands" Pg 24, line 23-24: delete "depending on the method of interpretation" Pg 24, line 24: delete "This negligible: : : company standard". Pg 25, line 3: insert "thus" before "affected" The authors agree and changes are made according proposals.

Pg 25, line 5: explain that DOC is a measure for NOM The authors replaced: "(DOC)" By: "(DOC, a measurement for natural organic matter)"

DWESD

8, C41–C48, 2015

Pg 25, line 5-6: replace “water matrix .. Meuse” by “the formation of bromate”. The authors agree and changes are made according proposal.

Pg 25, line 6-8: rephrase sentence, not clear what is meant. The authors replaced: “According to Croué et al. (1996) and Amy et al. (1993) bromate is formed proportionally when the ratio of ozone dose and DOC is exceeding 0.4mgO3/mgC and maximal contact times are applied. The ratio applied in this project is significantly lower than 0.4.” By: “Bromate is formed proportionally when the ratio of ozone dose and DOC, in mgO3/mgC, is exceeding 0.4 (Croué et al. 1996; Amy et al. 1993), which is much higher ratio than applied in this research.”

Pg 25, line 15: why you need to know the “minimum ozone/hydrogen peroxide ratio”? The authors don’t want to know the minimum ozone/hydrogen peroxide ratio. “minimum” is removed.

Pg 25, line 18:insert “accompanied by” before “with batch” Pg 25, line 22: Rephase as follows: “Thepilot plant consisted of an ozone loop reactor (Xylem Wedeco) with sequential injectionpoint (IPs) and sample points (SPs) and a degassing contact chamber, and an ozone generator. Pg 26, line 6, 9, 18: only use IP and SP Pg 26, line 10: replace “flowed out” by “discharged to” Pg 26, line 17: is = was Pg 26, line 22, 24, 25: was = is Pg 26, line 24: passed = passes Pg 27, line 1: rephrase sentence to “Because of the varying water quality, research over a : : :.” Pg 27, line 14: “representatively” = representativity Pg 27, line 17: replace “and” by “dosing” Pg 27, line 18: delete “RSF entered” Pg 27, line 20: rephrase into “about 0.1 mg CL-1, while the influent varied: : :.” Pg 28, line 11: use “50” instead of “Fifty” The authors agree and changes are made according proposals.

Pg 28, line 27-29: DOC is apparently measured as TOC, explain. Probably the definition of the analysis is wrong. The question cannot be answered at this moment (the co-author with the expert knowledge was not reached yet). I propose to answer this question later and continue the review process and implement the answer in the first

DWESD

8, C41–C48, 2015

review of the typeset manuscript.

Pg 29, line 4: delete “range” (it is one wavelength) Pg 29, line 20: delete “(resulting: : : atrazine)” The authors agree and changes are made according proposal.

Pg 29, line 23: also include the energy consumption for the production of hydrogen peroxide The authors agree that the comparison is not quite correct. We wanted to compare the energy consumption of ozone production with UV radiation generation. We replaced: “To achieve a similar atrazine conversion with a comparable pretreated surface water by applying UV/H2O2, the energy consumption is at least ten times higher (Lekkerkerker-Teunissen et al., 2013), which demonstrates the energy efficiency of the peroxone process.” By: “To achieve a similar atrazine conversion with a comparable pretreated surface water by applying UV/H2O2, with the same hydrogen peroxide dose, the energy consumption in order to generate UV radiation is at least ten times higher (Lekkerkerker-Teunissen et al., 2013), which demonstrates the energy efficiency of the peroxone process.”

Pg 29, line 26: if = when Pg 29, line 26 – pg 30: replace “the knowledge that bromate: : : ozone doses” by “ findings of Von Gunten (2003b) The authors agree and changes are made according proposals.

Pg 30, line 6: why 10 mg/L? elsewhere was mentioned 5 mg/L At an ozone dose of 5 mgL-1 and 5 mgL-1 hydrogen peroxide, the bromate concentration was about 16 μgL-1, higher than the WHO guideline of 10 μgL-1. With 10 mgL-1 hydrogen peroxide the bromate formation was lower than 10 μgL-1.

Pg 30, line 7: is= was Pg 30,line 8: rephrase by “to comply a bromate concentration below 0.5 _g L-1 at an ozone dose..” Pg 30, line 12: insert “dosing” before “was investigated” Pg 30, line 17: replace “year” by “period” (longer than year) Pg 30, line 18: differs = differed Pg 30, line 23: rephrase into “peroxide, exceeded the value of 0.5 _g L-1 (with a maximum of 1.0 _gL-1) Pg 31, line 4: appoint = indicate Pg 31, line 6: replace “from.. 2012” by “during the test period” Pg 31, line 11: Croué = Croué et al.

DWESD

8, C41–C48, 2015

Pg 31, line 13: “was found” = is The authors agree and changes are made according proposals.

Pg31, line 15-16: There is or is not a correlation. You cannot say “correlation is not very obvious” The authors replaced: “A correlation between bromate and bromide was not very obvious, although the dependency of the bromide concentration is known and expected at bromide concentrations higher than 20 μgL-1 (Gottschalk et al., 2010).” By: “The bromate concentration increased with increasing bromide concentration which is expected at bromide concentrations higher than 20 μgL-1 (Gottschalk et al., 2010).”

Pg 31, line 17-18: delete “It is: : :.bromide alone” Pg 31, line 22-23: delete “At higher pH: : : bromate formation” (it is clear from the small variation that you cannot draw conclusions) Pg 31, line 24-27: delete “and: : :.. probably preferential”. (see above) Pg 32, line 1: replace “To which extent: : : .For sure” by “Probably” Pg 32, line 8: replace RSF by “the influent” Pg 32, line 9: is=was Pg 32, line 11: delete “Concerning the enclosed Meuse” Pg 32, line 15: delete “under which: : : negligible” Pg 32, line 18: delete second “the” Pg 32, line 20: delete “enormously” Pg 32, line 25: is = was The authors agree and changes are made according proposals.

Pg 32, line 26: mention all model compounds of relevance The authors replaced: “metformin till diglyme” By: ” metformin, atrazine, iopromide and diglyme”

Pg 33, line 3: rephrase into “agent, also contains an aromatic ring, but: : :.” The authors agree and changes are made according proposal.

Pg 33, line 6: mention all model compounds of relevance The authors replaced: “ibuprofen to phenazone” By: “ibuprofen, metoprolol, bentazone, isoproturon and phenazone”

Pg 33, line 18: rephrase into “Bromacil was thus directly oxidized..” Pg 33, line 23: delete “ Besides: : :. 6 mgL-1” Pg 34, line 2: will be = is Pg 34, line 5: delete sentence Pg 34, line 7: easy = easily Pg 34, line 11: delete “therefore” Pg 34, line 12: substitute

DWESD

8, C41–C48, 2015

"Dunea guideline" by "value of 0.5 _gL-1 Pg 34, line 15-18: delete paragraph Pg 34, line 19: rephrase into "It should therefore be noted: : :" Pg 34, line 21-22: delete "In the first: : :.Secondly" Pg 34, line 22-23: rephrase into "Also because oxidation by peroxone leads: : :products of OMPs: : : Sonntag et al. (2012), that may have unwanted toxic properties". The authors agree and changes are made according proposals.

Pg 34, line 27 – Pg 35 line 2: delete paragraph The authors find it relevant to maintain the paragraph, together with the paragraph above. In our opinion it is important to mention that unwanted reaction products can be formed. We ourselves are aware of that and if we had no additional biological treatment and PAC adsorption, we do not consider to apply this peroxone process. We hope you understand our opinion.

Pg 35, line 5: RSF = influent Pg 35, line 10-14: delete sentences "All three: : :. Co-correlation." Pg 35, line 15-16: delete "The fact: : : DOC concentration and rephrase into ", with the practical implication that in summer: : :dose needs to be : : :.. bromate formation." (so coming after "Fig 7") Pg 35, line 24: degrades = degraded Pg 36, line 2-4: delete " In drinking water: : :. Guideline for bromate" Pg 36, line 5: is = was Pg 36, line 6: is = was Pg 36, line 7: has = had Pg 36, line 8: limits = limited Pg 36, line 8: add "to levels below 0.5 _gL-1 The authors agree and changes are made according proposals.

Kind regards, Antonie Knol, on behalf of the co-authors

Please also note the supplement to this comment:
http://www.drink-water-eng-sci-discuss.net/8/C41/2015/dwesd-8-C41-2015-supplement.pdf

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