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Accounting for bioavailability in the aquatic risk assessment of metals



P001 QMS ISO 14 RED REGISTER Graham Merrington



Introduction

- Challenges assessing metal environmental risks
- What is bioavailability and why account for it in risk assessment?
- Biotic ligand models.....
- User-friendly tools
- What do you need?
- Some examples.....
- Queries and questions: common problems and issues...



Challenges assessing metal environmental risks

- Metals are ubiquitous
- Can change chemical form in response to water chemistry
- The form of the metal influences the ecotoxicity to aquatic organisms
- Some metals are essential for the functioning of biological systems
- One limit value doesn't fit all situations







What is bioavailability?



combination of the physico-chemical factors in the water column governing metal behaviour and the biological receptor - its specific pathophysiological characteristics (?)



Why account for bioavailability in environmental risk assessment?



Predicted 'stylised' changes in the ecotoxicity of nickel, expressed as an HC5, for pH, Ca (mg l⁻¹) and DOC (mg l⁻¹). Individual parameters were varied while the other two parameters remained constant (pH 7, Ca 120 mg l⁻¹, DOC 2 mg l⁻¹).



Predicted variation in copper toxicity (HC5) µg Cu l⁻¹) as a function of pH and DOC in soft water.



Hazardous Concentrations µg

Why account for bioavailability in environmental risk assessment?



| System | Canadian Shield Lake | Lake Ontario | Desjardin Canal |
|---|-------------------------------------|---------------------------------------|---------------------------------------|
| Characteristics | Hardness: 4 mg CaCO ₃ | Hardness: 124 mg CaCO ₃ | Hardness: 318 mg CaCO ₃ |
| | DOC: 6 mg/L | DOC: 1.1 mg/L | DOC: 5.8 mg/L |
| | pH: 6.5 | pH: 8.2 | pH: 7.7 |
| Hardness-based WQG (Current approach) | 25 µg Ni/L | 112 µg Ni/L | 150 μg Ni/L |
| Hardness-based Rank Order | 1 | 2 | 3 |
| Bioavailability- based EQS (direct application of EU approach to Canadian waters) | 16.3 µg Ni/L | 4 µg Ni/L | 11.3 µg Ni/L |
| Bioavailability- based Rank Order | 3 | 1 | 2 |

•Hardness based approaches may not be reaching the appropriate conclusions

Biotic ligand models

- Gill Surface Interaction Model Pagenkopf 1983
 - » Describes interaction of metals with fish gills (the sites of toxic action) and competition from other ions
- Humic Ion Binding Model V Tipping 1992
 - » Describes binding of metals with natural organic matter and competition from other ions
- Biotic Ligand Model Di Toro 2001
 - » Combines both of these models to describe toxicity as a function of water chemistry
- Competition and complexation effects are critical in being able to describe the effect of a metal as a function of water quality.

Biotic ligand models (continued)

- These BLM describes competitive interactions for binding by DOC and the biotic ligand.
- Can quantitatively relate binding to <u>chronic</u> toxicity (fractional occupancy at EC10)
- But....these models are quite complex, require in-depth understanding to use
- Data input requirement (> 10 physicochemical water parameters)
- They are very robust tools to make predictions, but complex andbeautiful



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User-friendly tools





- Need a way to mimic the BLM outputs
- Using a reduced number of inputs
- In a package the runs on routine office software
- With loss of accuracy likely to lead to a precautionary assessment
- The output needs to be....understandable and useable!
- Back in 2007, the Environment Agency of England and Wales commissioned wca to develop userfriendly tools for copper and zinc....

What do you need?



- Two tools are available M-BAT (the UK Environment Agency's) and Bio-met.
- Both are based on chronic ecotoxicity data and the outputs of the different BLMs for Cu, Ni, Zn (and Mn in the case of M-BAT)
- Key input parameters are for matched (taken from the same sample at the same time) dissolved
 organic carbon (DOC), pH and calcium/hardness
- All three are needed

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| "User-friendly" Bio | otic Ligand Model Version 3.0 - December 2015 | |
| Please register at www.bio-met | net to ensure you're using the most recent version of the tool | |
| Start | About this tool | |
| Help | This software tool estimates the potential risk to the aquatic environment posed by copper, nickel and zinc after considering bioavailability . The tool will calculate Local EQS values and Bioavailable Metal Concentrations based on information on local water physicochemistry. This tool has been developed as part of the <i>bio-met project</i> and has been designed to operate in Microsoft Excel 2007 and 2010. A web-based version | |
| Glossary | of this tool, together with a fuller description of the science underpinning the tool, a description of the tool's operation and validation, case studies and comprehensive guidance on its use are available at www.bio- | |
| Generic EQS Bioavailable | met.net. This software tool is based on calculations from Biotic Ligand Models. It is currently only applicable for use in | |
| Login | European freshwaters and is intended to be used as part of tiered risk assessment or as an early tier in compliance assessment. | |
| Hints and Tips | How to use this tool | |
| You can enter data for up to 2000 samples. Make sure that each | Please read these instructions carefully before you start. Further guidance on using this tool can be obtained by visiting www.bio-met.net | |
| Introduction | Sheet1 (+) | X k |
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Data Input & Results

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| Back | | | | | | | | | | | | | | |
| Samples Processed 0 | | | | | | | | | | | | | | |
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| 1 | 1.3 | 4 | 8 | 1.7 | 65.6 | 1 | 3.70 | 0.27 | 0.27 | 0.27 | 1 | 4.00 | 1.00 | 1.30 | 0.33 | Y | 20.06 | 0.54 | 2.17 | 0.20 | 1 | 4 |
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| 0.52 | 0.35 | 2.11 | 6.81 | 1.1 | 8.15717 | 1 | 3.82 | 0.26 | 0.14 | 0.14 | | 8.90 | 0.45 | 0.16 | 0.04 | | 11.90 | 0.92 | 1.93 | 0.18 | \$ | 1 |
| 0.55 | 0.17 | 3.32 | 7.05 | 3.9 | 11.8104 | 1 | 20.87 | 0.05 | 0.03 | 0.03 | 1 | 12.23 | 0.33 | 0.06 | 0.01 | | 23.89 | 0.46 | 1.51 | 0.14 | | 4 |
| 17 | 1.02 | 4.11 | 6.85 | 13.3 | 18.5163 | 1 | 55.23 | 0.04 | 0.03 | 0.03 | 3 | 23.57 | 0.21 | 0.14 | 0.04 | | 44.10 | 0.35 | 1.02 | 0.03 | | 1 |
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| 7.02 | 2,1 | 25.5 | 7.89 | 3.15 | 68.8 | 1 | 7.90 | 0.13 | 0.89 | 0.83 | 9 | 5.82 | 0.69 | 1.44 | 0.36 | | 28.45 | 0.38 | 9.77 | 0.90 | | 4 |
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| 0.8 | 0.4 | 2 | 6.68143 | 0.51 | 3.02688 | 3 | 1.59 | 0.63 | 0.50 | 0.50 | Y | 9.06 | 0.44 | 0.18 | 0.04 | Y | 11.90 | 0.92 | 1.83 | 0.17 | Y | 1 |
| 0.6 | 0.3 | 1.2 | 6.4625 | 0.45 | 2.43611 | 1 | 1.00 | 1.00 | 0.60 | 0.60 | Y | 9.86 | 0.41 | 0.12 | 0.03 | Y | 11.90 | 0.92 | 1.10 | 0.10 | Y | - |
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| 3.22 | 1.22 | 24.7 | 7.96595 | 3.165 | 86,419 | 1 | 7.90 | 0.13 | 0.41 | 0.4 | 1 | 5.82 | 0.69 | 0.84 | 0.21 | | 29.27 | 0.37 | 9.20 | 0.84 | ŧ | |
| 3.74 | 4.45 | 16.8 | 7.64 | 7.82 | 7.7 | 1 | 35.48 | 0.03 | 0.11 | 0.1 | 1 | 15.12 | 0.26 | 1.18 | 0.29 | | 74.89 | 0,15 | 2.45 | 0.22 | 2 | ÷ |

Sheet1 Results

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| Optional Measured Copper Conc (dissolved) [µg/L] | Optional Measured Nickel Conc (dissolved) [µg/L] | Detional Measured Zinc Conc (dissolved) [µg/L] | Required pH | Required DOC [mg/L] | Ca [mg/L] | Optional Zinc ABC Conc (dissolved) [µg/L] | Local EQS (dissolved) [µg/L] | BioF | Bioavailable Copper Conc [µg/L] | RCR | Notes | Local EQS (dissolved) [µg/L] | BioF | Bioavailable Nickel Conc (ug/L) | RCR | Notes | Local EQS (dissolved) [µg/L] | BioF | Bioavailable Zinc Conc (µg/L) | RCR | Note |
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| 1 | 1.3 | 4 | 8 | 1.7 | 65.6 | 1 | 3.70 | 0.27 | 0.27 | 0.27 | | 4.00 | 1.00 | 1.30 | 0.33 | Y | 20.06 | 0.54 | 2.17 | 0.20 | |
| 3 | 2.4 | 3 | 8.5 | 0.8 | 42.2 | 1 | 1.13 | 0.89 | 2.66 | 2.66 | | 4.00 | 1.00 | 2.40 | 0.60 | Y | 12.87 | 0.85 | 2.54 | 0.23 | 4 |
| 0.52 | 0.35 | 2.11 | 6.81 | 1.1 | 8.15717 | 1 | 3.82 | 0.26 | 0.14 | 0.14 | | 8.90 | 0.45 | 0.16 | 0.04 | | 11.90 | 0.92 | 1.93 | 0.18 | |
| 0.55 | 0.17 | 3.32 | 7.05 | .3.9 | 11.8104 | 1 | 20.87 | 0.05 | 0.03 | 0.03 | | 12.20 | 0.00 | 0.06 | 2.5 | | 23.89 | 0.46 | 1.51 | 0.14 | |
| 0.41 | 0.68 | 2.85 | 6.61 | 9.5 | 5.95524 | 1 | 28.22 | 0.04 | 0.01 | 0.01 | - | 19.22 | 0.21 | 0.14 | 0.04 | | 33.45 | 0.33 | 0.93 | 0.03 | |
| 17 | 1.02 | 4.11 | 6.85 | 13.3 | 18.5163 | 1 | 55.23 | 0.02 | 0.03 | 0.03 | - | 23.57 | 0.17 | 0.17 | 0.04 | | 44.10 | 0,25 | 1.02 | 0.05 | - |
| 7.02 | 2.1 | 25.5 | 7.89 | .3.15 | 68.8 | 1 | 7.90 | 0.13 | 0.89 | 0.89 | | 5.82 | 0.69 | 1.44 | 0.36 | | 28.45 | 0.38 | 9.77 | 0.90 | |
| 5.08 | 1.5 | 19.9 | 7.67 | 5.21 | 75.1 | 1 | 16.94 | 0.06 | 0.30 | 0.30 | | 8.69 | 0.46 | 0.69 | 0.17 | | 37,48 | 0.29 | 5.79 | 0.53 | |
| | | | | | | 1 | | | | | | | | | | | | | | | |
| 0.8 | 0.4 | 2 | 6.68143 | 0.51 | 3.02688 | 1 | 1.59 | 0.63 | 0.50 | 0.50 | Y | 9.06 | 0.44 | 0.18 | 0.04 | Y | 11.90 | 0.92 | 1.83 | 0.17 | Y |
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| MONITORING) | DATA | | | 1 | | | | RESI | ULTS (Copper) | | _ | | RESU | JLTS (Nickel) | - | | - | RES | ULTS (Zinc) | | |
| Optional Measured Copper Conc (dissolved) [µg/L] | Optional Measured Nickel Conc (dissolved) [µg/L] | Detional Measured Zinc Conc (dissolved) [µg/L] | Required pH | DOC [mg/L] | Ca [mg/L] | Optional Zinc ABC Conc (dissolved) [µg/L] | Local EQS (dissolved) [µg/L] | BioF | Bioavailable Copper Conc [µg/L] | RCR | Notes | Local EQS (dissolved) [µg/L] | BioF | Bioavailable Nickel Conc (µg/L) | RCR | Notes | Local EQS (dissolved) [µg/L] | BioF | Bioavailable Zinc Conc (µg/L) | RCR | Note |
| 0.7 | 1.1 | 1.4 | 7.8 | 0.3 | 8.2 | 1 | 1.07 | 0.94 | 0.65 | 0.65 | | 4.00 | 1.00 | 1.10 | 0.28 | Y | 11.90 | 0.92 | 1.28 | 0.1 | 2 |
| 1 | 1.3 | 4 | 8 | 1.7 | 65.6 | 1 | 3.70 | 0.27 | 0.27 | 0.27 | - | 4.00 | 1.00 | 1.30 | 0.33 | Y | 20.06 | 0.54 | 2.17 | 0.20 | 0 |
| 3 | .2.4 | 3 | 8.5 | 0.8 | 42.2 | 1 | 1.13 | 0.89 | 2.66 | 2.66 | | 4.00 | 1.00 | 2.40 | 0.60 | Y | 12.87 | 0.85 | 2.54 | 0.23 | 3 |
| 0.52 | 0.35 | 2.11 | 6.81 | 1.1 | 8.15717 | 1 | 3.82 | 0.26 | 6 0.14 | 0.14 | | 8.90 | 0.45 | 0.16 | 0.04 | | 11.90 | 0.92 | 1.93 | 0.1 | 8 |
| 0.55 | 0.17 | 3.32 | 7.05 | .3.9 | 11.8104 | 1 | 20.87 | 0.05 | 5 0.03 | 0.03 | | 12.23 | 0.33 | 0.06 | 0.01 | | 23.89 | 0.46 | 1.51 | 0.1 | 4 |
| 0.41 | 0.68 | 2.85 | 6.61 | 9.5 | 5.95524 | 1 | 28.22 | 0.04 | 0.01 | 0.01 | | 19.22 | 0.21 | 0.14 | 0.04 | | 33.45 | 0.33 | 0.93 | 0.0 | Э |
| 17 | 1.02 | 4.11 | 6.85 | 13.3 | 18.5163 | 1 | 55.23 | 0.02 | 2 0.03 | 0.03 | - | 23.57 | 0.17 | 0,17 | 0.04 | | 44.10 | 0,25 | 1.02 | 0.0 | 3 |
| 7.02 | 21 | 25.5 | 7.89 | 3.15 | 68.8 | 1 | 7.90 | 0.13 | 0.89 | 0.89 | - | 5.82 | 0.69 | 1.44 | 0.36 | | 28.45 | 0.38 | 9.77 | 0.9 | 0 |
| 5.08 | 1.5 | 19.9 | 7.67 | 5.21 | 75.1 | 1 | 16.94 | 0.06 | 0.30 | 0.30 | | 8.69 | 0.46 | 0.69 | 0.17 | | 37.48 | 0.29 | 5.79 | 0.5 | 3 |
| | | | | | | 1 | | | | | | | | | | | | | | | |
| 0.8 | 0.4 | 2 | 6.68143 | 0.51 | 3.02688 | 1 | 1.59 | 0.63 | 0.50 | 0.50 | Y | 9.06 | 0.44 | 0.18 | 0.04 | Y | 11.90 | 0.92 | 1.83 | 0.17 | / Y |
| 0.5 | 0.3 | 1.2 | 6.4625 | 0.45 | 2.43611 | 1 | 1.00 | 1.00 | 0.50 | 0.60 | Y V | 9.86 | 0.41 | 0.12 | 0.03 | Y | 11.90 | 0.92 | 1.10 | 0.10 | |
| 0.7 | 0.5 | 2.1 | 7.59375 | 0.44 | 10.3229 | 1 | 1.00 | 0.86 | 0.10 | 0.10 | | 4.00 | 1.00 | 0.20 | 0.05 | Y | 11.90 | 0.92 | 1.33 | 0.21 | 8 |
| | | | | | | 1 | | | | | | | | | | | | | | | |
| 3.22 | 1.22 | 24.7 | 7.96595 | 3.165 | 86,419 | 1 | 7.90 | 0,13 | 8 0.41 | 0.41 | | 5.82 | 0.69 | 0.84 | 0.21 | | 29.27 | 0.37 | 9.20 | 0.8 | 4 |
| 3.74 | 4.45 | 16.8 | 7.64 | 7.82 | 7.7 | 1 | 35.48 | 0.03 | 0.11 | 0.11 | | 15.12 | 0.26 | 1.18 | 0.29 | | 74.89 | 0,15 | 2.45 | 0.22 | 2 |
| | Sheet1 | Results | Ð | | | | | | | | | | | | | | * | | | | Þ |
| Ready | | | | | | | _ | | | | | | | | | | 田同 | ш | 4 1 | | + 95% |

| 8 | | ÷ | | | | | Сору о | f Bio-m | et_bioavailability | /_tool_v | 3.03_04-0 | 01-2016 - Excel | | | | | | | m – | ٥ | × |
|--|--|--|--------------------------|---------------------------|-----------------------------|---|------------------------------------|-----------------|---------------------------------------|------------------------|-----------------------------|--|---------------------------|---------------------------------------|--------|-------|------------------------------------|------|-------------------------------------|------|-------|
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| IONITORING) | DATA | | | | | | | RESU | ILTS (Copper) | | | | RESI | ULTS (Nickel) | | | | RES | ULTS (Zinc) | | |
| Opiienal Measured Copper Conc (dissolved) [µg/L] | Optional Measured Nickel Conc (dissolved) [µg/L] | Detional Measured Zinc Conc (dissolved) [µg/L] | Required pH | Required DOC [mg/L] | Required Ca [mg/L] | Optional Zinc ABC Conc (dissolved) [µg/L] | Local EQS (dissolved) [µg/L] | BioF | Bioavailable Copper Conc [µg/L] | RCR | Notes | Local EQS (dissolved) [µg/L] | BioF | Bioavailable Nickel Conc (µg/L) | RCR | Notes | Local EQS (dissolved) [µg/L] | BioF | Bioavailable Zinc Conc (µg/L) | RCR | Not |
| 0.7 | ti | 1.4 | 7.8 | 0.3 | 8.2 | 1 | 1.07 | 0.94 | 0.65 | 0.65 | ; | 4.00 | 1.00 | 1.10 | 0.28 | Y | 11.90 | 0.92 | 1.28 | 0.12 | |
| 1 | 1.3 | 4 | 8 | 1.7 | 65.6 | 1 | 3.70 | 0.27 | 0.27 | 0.27 | , | 4.00 | 1.00 | 1.30 | 0.33 | Y | 20.06 | 0.54 | 2.17 | 0.20 | _ |
| | 2.4 | | 0.0 | 0.0 | 76,6 | 1 | . 19 | 0.00 | 2.00 | 2.00 | | 4.00 | 1.00 | 2.40 | 0.00 | | 12.01 | 0.05 | 2.07 | 0.20 | |
| 0.52 | 0.35 | 2.11 | 6.81 | 1.1 | 8.15717 | 1 | 3.82 | 0.26 | 0.14 | 0.14 | - | 8.90 | 0.45 | 0.16 | 0.04 | | 11.90 | 0.92 | 1.93 | 0.18 | |
| 0.55 | 0.17 | 3.32 | 7.05 | 3.9 | 11.8104 | | 20.87 | 0.05 | 0.03 | 0.03 | 1 | 12.23 | 0.33 | 0.06 | 0.01 | | 23.89 | 0.46 | 1.51 | 0.09 | _ |
| 17 | 1.02 | 4.11 | 6.85 | 13.3 | 18.5163 | 1 | 55.23 | 0.02 | 0.03 | 0.03 | | 23.57 | 0.21 | 0.17 | 0.04 | | 44.10 | 0.05 | 1.02 | 0.09 | |
| | | | | 1 | | 1 | | | | | | | | - | | | | | | _ | |
| 7.02 | 2,1 | 25.5 | 7.89 | 3.15 | 68.8 | 1 | 7.90 | 0.13 | 0.89 | 0.89 | | 5.82 | 0.69 | 1.44 | 0.36 | | 28.45 | 0.38 | 9.77 | 0.90 | |
| 5.08 | 1.5 | 19.9 | 1.67 | 5.21 | (5,1 | 1 | (6,34 | 0.06 | 0.30 | 0.30 | | 0.03 | 0.46 | 0.63 | 0.17 | - | 37,48 | 0.29 | 5.73 | 0.53 | _ |
| 0.8 | 0.4 | 2 | 6.68143 | 0.51 | 3.02688 | 1 | 1.59 | 0.63 | 0.50 | 0.50 | Y | 9.06 | 0.44 | 0.18 | 0.04 | Y | 11.90 | 0.92 | 1.83 | 0.17 | Y |
| 0.6 | 0.3 | 1.2 | 6.4625 | 0.45 | 2.43611 | 1 | 1.00 | 1.00 | 0.60 | 0.60 | Y | 9.86 | 0.41 | 0.12 | 0.03 | Y | 11.90 | 0.92 | 1.10 | 0.10 | Y |
| 0.7 | 0.5 | 2 | 6.2825 | 0.44 | 2.03353 | | 1.00 | 1.00 | 0.70 | 0.70 | Y | 9.86 | 0.41 | 0.20 | 0.05 | Y | 11.90 | 0.92 | 2.93 | 0.27 | Y |
| 0.2 | 0.8 | 2.1 | 7,59375 | 0.33 | 10.3229 | | 1.17 | 0.86 | 0.17 | 0.17 | | 4.00 | 1.00 | 0.80 | 0.20 | Y | 11.90 | 0.92 | 1.92 | 0.18 | - |
| 3.22 | 1.22 | 24.7 | 7.96595 | 3.165 | 86.419 | 1 3 | 7.90 | 0.13 | 0.41 | 0.41 | 1 | 5.82 | 0.69 | 0.84 | 0.21 | | 29.27 | 0.37 | 9.20 | 0.84 | |
| 3.74 | 4.45 | 16.8 | 7.64 | 7.82 | 7.7 | 1 | 35.48 | 0.03 | 0.11 | 0.11 | 1 | 15.12 | 0.26 | 1.18 | 0.29 | | 74.89 | 0,15 | 2.45 | 0.22 | |
| | Sheet1 | Results | ۲ | | | | | | | | | | | | | | | | | | • |
| Ready | | | | | | | | | | | | | | | | | 田面 | Ш | | - + | 95% |

Queries and questions....

Only covers freshwaters (at the moment!) Built in EQS (WQG) for long-term exposures Regulatory tool NOT a replacement for the **BLMs**



a

Validated boundaries



Validation ranges.....

| Metal | рН | Ca, mg L ⁻¹ | DOC, mg L ⁻¹ |
|-------|-----------|------------------------|-------------------------|
| Cu | 6.0-8.5 | 3.1-93 | Unlimited |
| Ni | 6.5-8.2 | 2.0-88* | Unlimited |
| Zn | 6.0-8.(2) | 2.0-160 | Unlimited |

- Determined by the ranges over which the ecotoxicity tests have been performed.
- Validated in the field too!

Summary

- Accounting for bioavailability of trace elements reflects what the aquatic organism actually "experiences".
- Simplified tools allows local assessment of potential metal risks
- These tools are already being used by regulators well validated
- Provides an evidence-base for decision making
- As with soils though be wary of using WQG or EQS from other jurisdictions!









Questions?

Some useful (?) material.

http://bio-met.net

- <u>http://www.wfduk.org/search/Bioavailability</u>
- <u>https://www.nickelinstitute.org/en/MediaCentre/</u> <u>News/CurrentYear/20160205-Bioavailability.aspx</u>
- <u>http://bio-met.net/wp-content/uploads/FINAL-</u>
 <u>TECHNICAL-GUIDANCE-TO-IMPLEMENT-</u>
 <u>BIOAVAILABILITYNovember-20142.pdf</u>

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