MP UV/H_2O_2 treatment for organic contaminant control and byproduct mitigation

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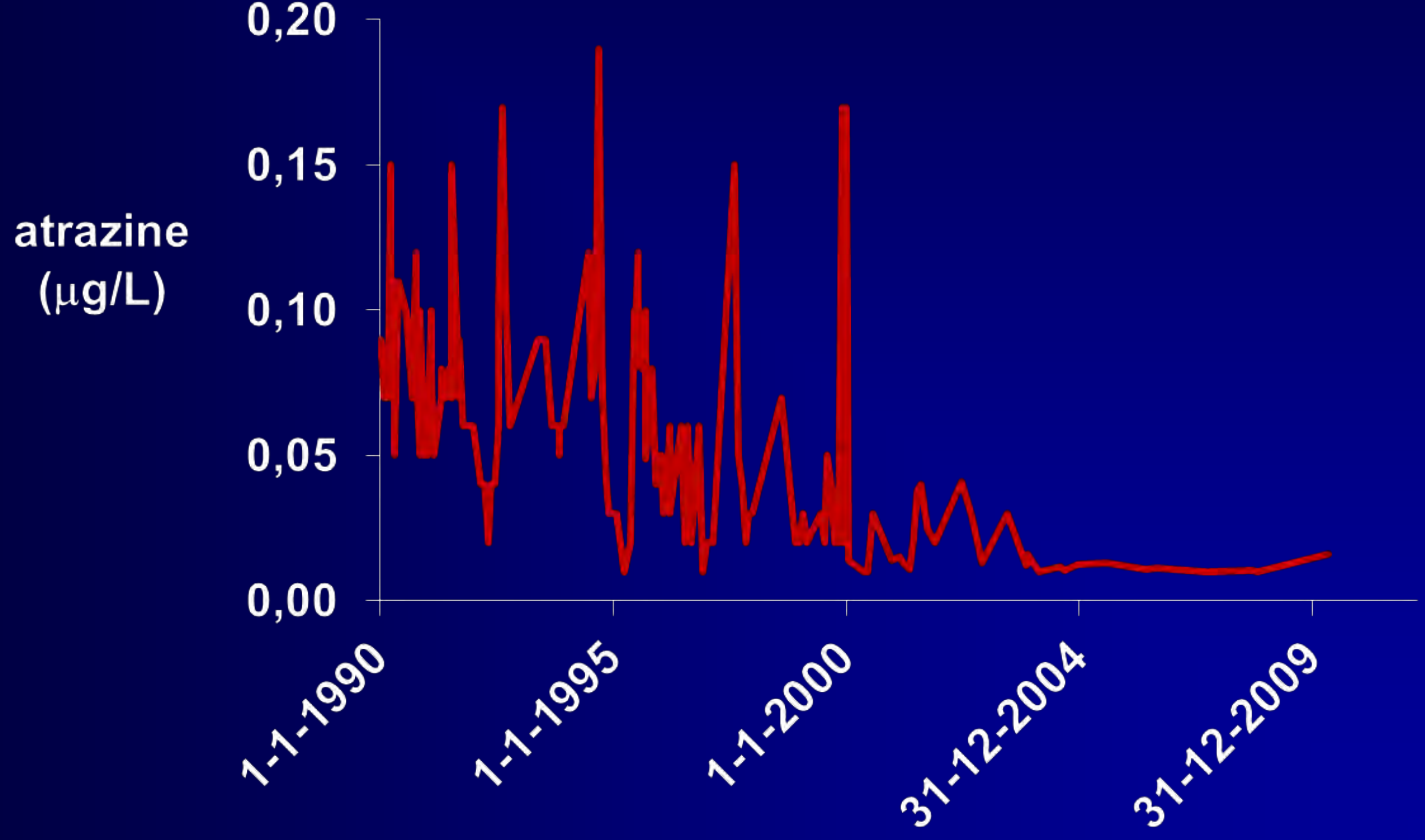
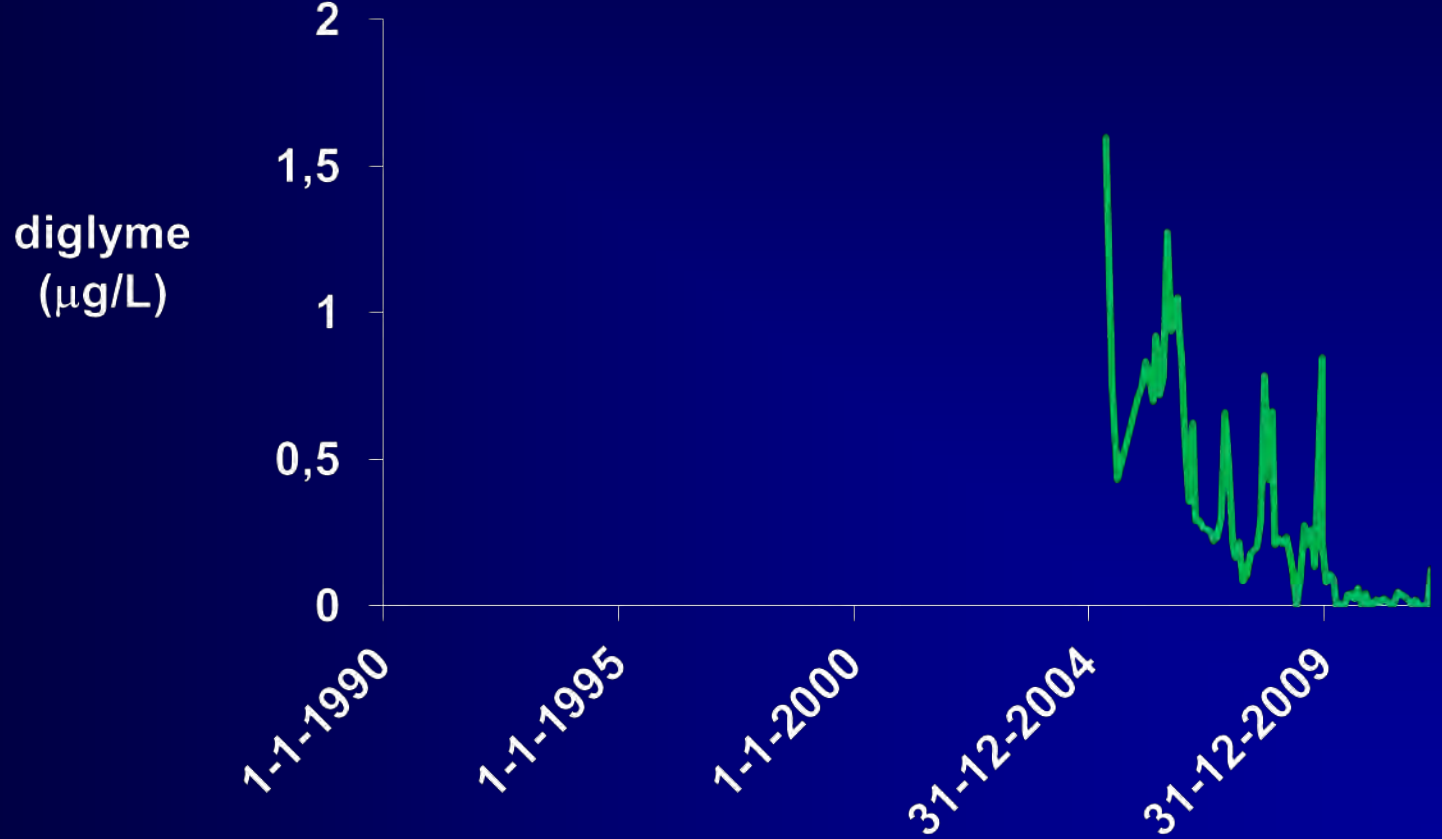
http://nl.wikipedia.org/wiki/Bestand:Flusssystemkarte_Rhein_06.jpg

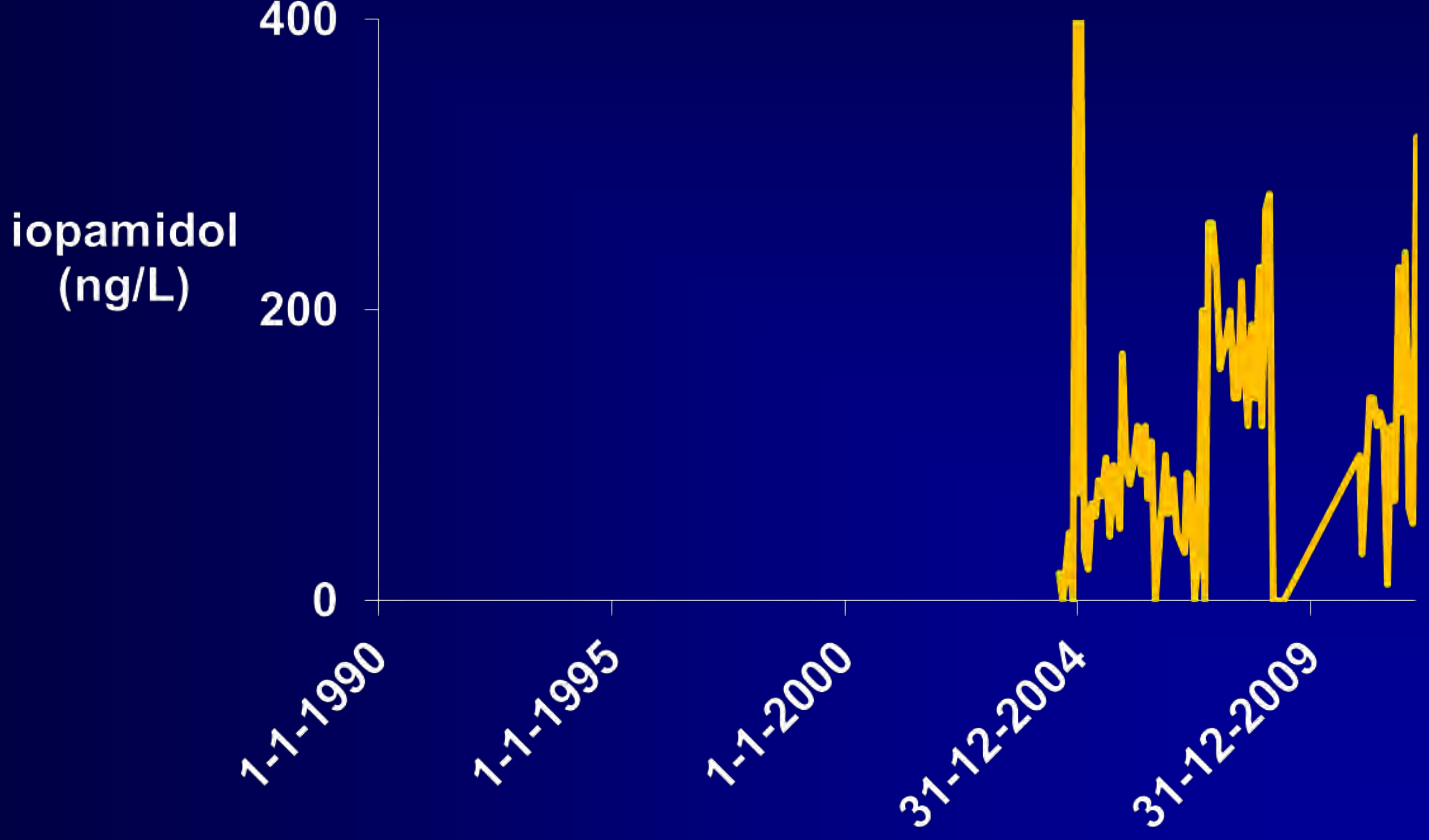
pesticide atrazine in IJssel Lake water



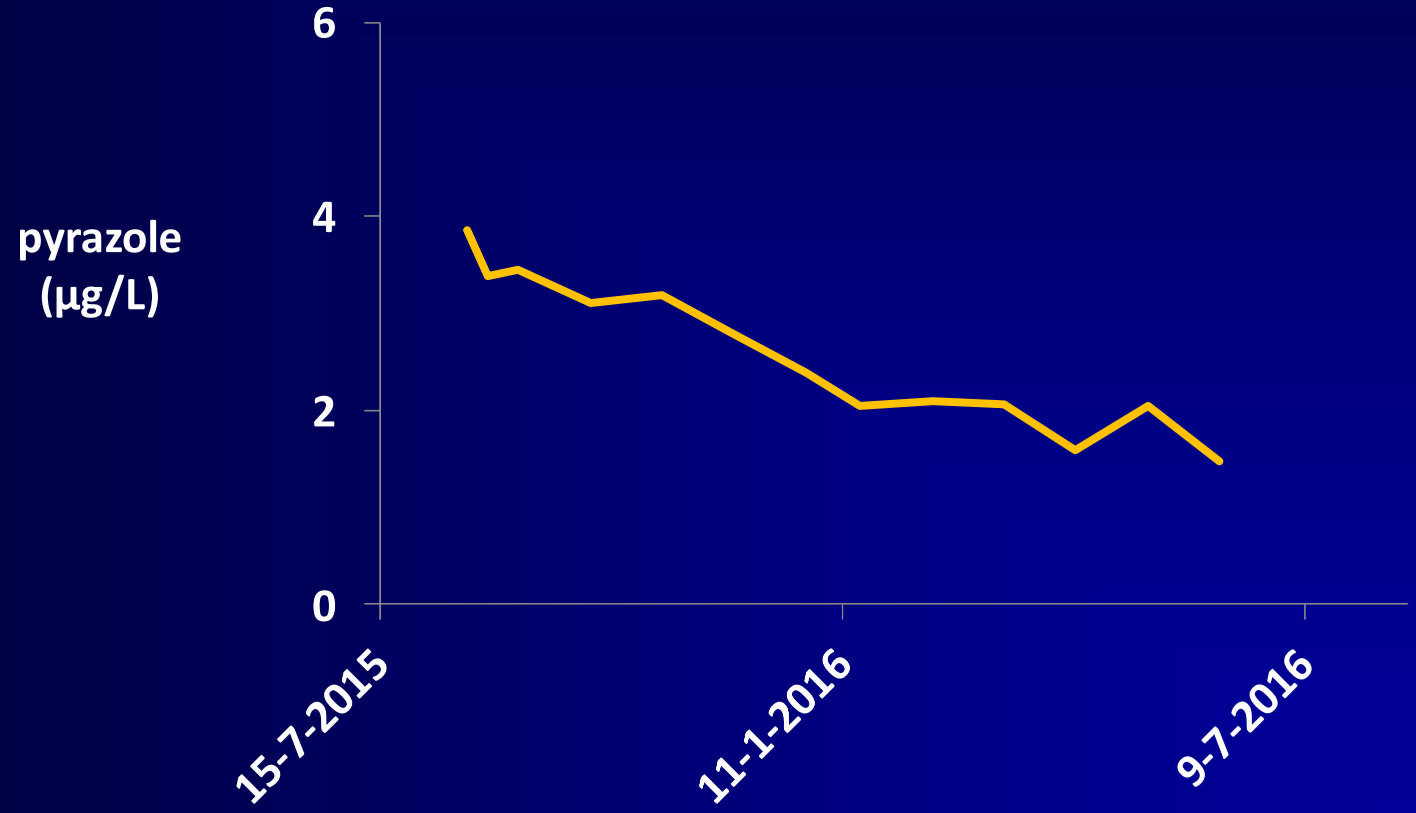
solvent diglyme in IJssel Lake water



röntgen contrast media in IJssel Lake water



pyrazole in IJssel Lake water due to discharge in Rhine



micropollutants and advanced drinking water treatment

- drugs, pharmaceuticals, pesticides, industrial compounds in drinking water (sources) always give rise to media attention

- contribution via industrial and domestic waste water and run off

- drinking water companies to address this in technology and communications

Ineos darf weniger Pyrazol in den Rhein leiten

Von Stefan Schneider

Laut einer neuen amtlichen Bewertung könnte die Chemikalie trinkwassergefährdend sein.

Dormagen. Das Petrochemie-Unternehmen Ineos muss bei der Einleitung seiner Abwässer in den Rhein nachbessern. Das hat die Bezirksregierung Köln dem Konzern auferlegt. Hintergrund sind Funde der Chemikalie Pyrazol im Rhein, die das Landesumweltamt (LANUV) auf den Plan

Facing the Yuck Factor

FEATURE ARTICLE - September 17, 2007 *by Peter Friederici*

Facing the yuck factor. PAUL LACHINE

How has the West embraced water recycling? Very (gulp) cautiously

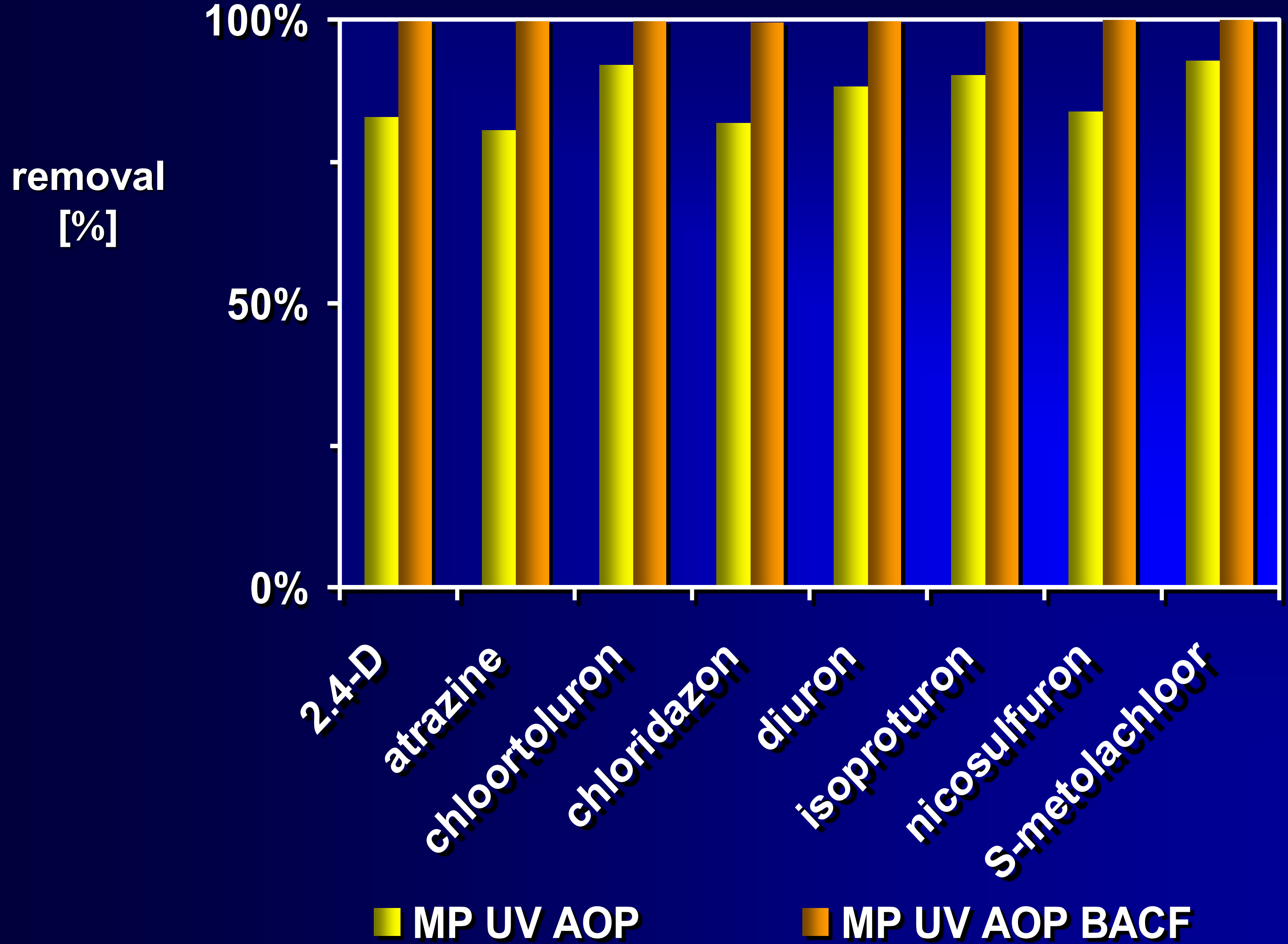
robust multibarrier approach

- organic contaminants are ‘moving target’
  - they move faster than technology development and implementation
  - toxicity, mixture toxicity, contribution via water, regulator, public perception; all influence discussion

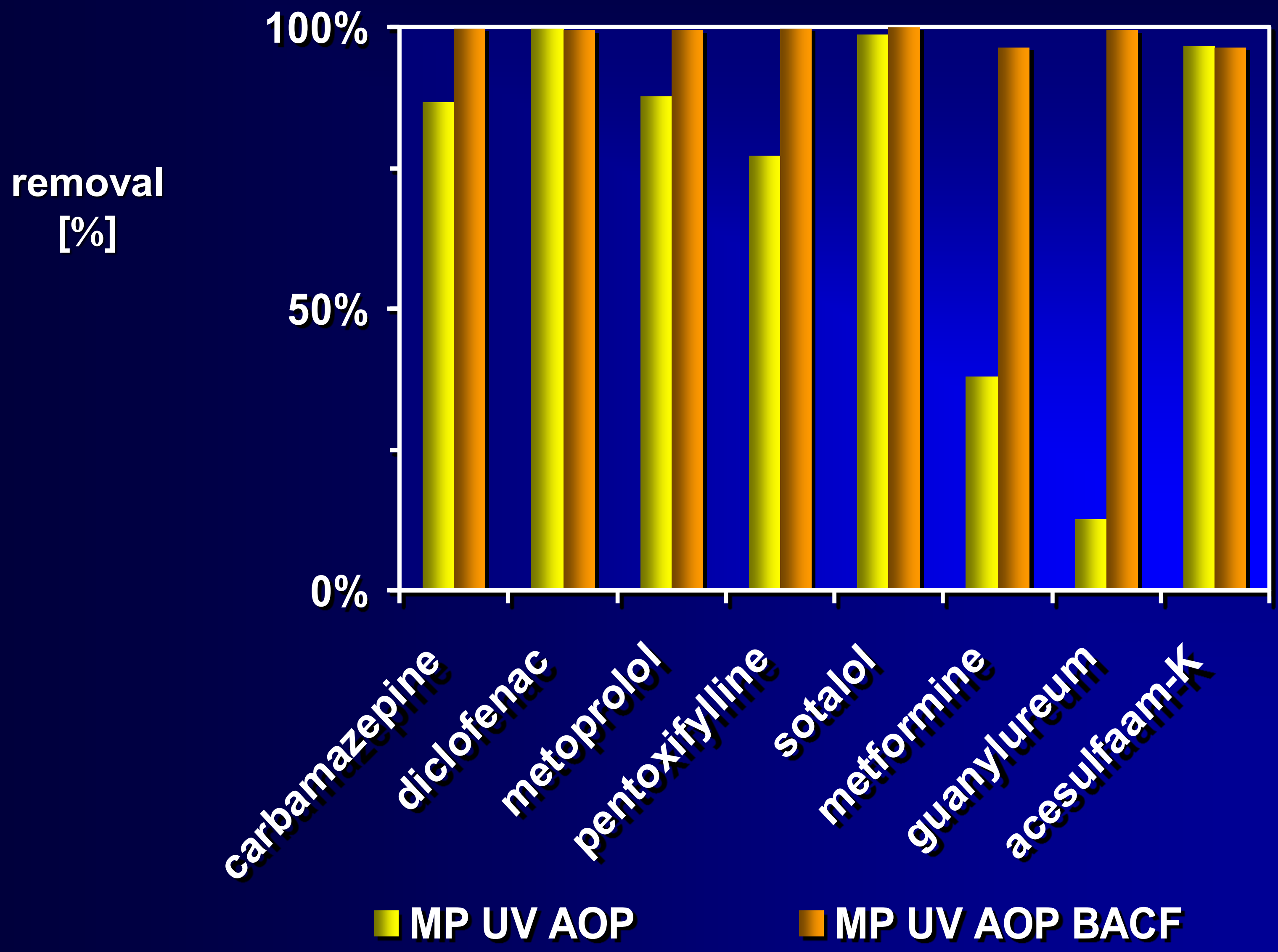
- justifies non selective multibarrier approach against organic micropollutants for PWN
  - oxidative treatment: MP UV/H_2O_2 process
  - adsorptive posttreatment by biological activated carbon filtration (BACF)


SWIFT

MP UV AOP and BACF (herbicides, summer)



MP UV AOP and BACF (pharmaceuticals, summer)



MP UV/H_2O_2 reliable barrier for organic contaminant control in a multibarrier treatment approach

advanced oxidation and byproduct formation

- **advanced oxidation of micro pollutants**
  - **mineralisation rarely applied**
  - **formation metabolites from target pollutants**
  - **risk of harmful daughter compounds**

- **advanced oxidation of matrix constituents**
  - **matrix: natural organic mater, inorganics**
  - **undesired reactions may form harmful byproducts**
    - ozone: bromate
    - UV: none?

MP UV/H_2O_2 and byproduct formation from matrix constituents

- chemical analysis and literature
  - photolysis of nitrate to nitrite
  - formation biodegradable organic carbon
  - nothing harmful identified by chemical analysis

- general perception: no harmful byproducts

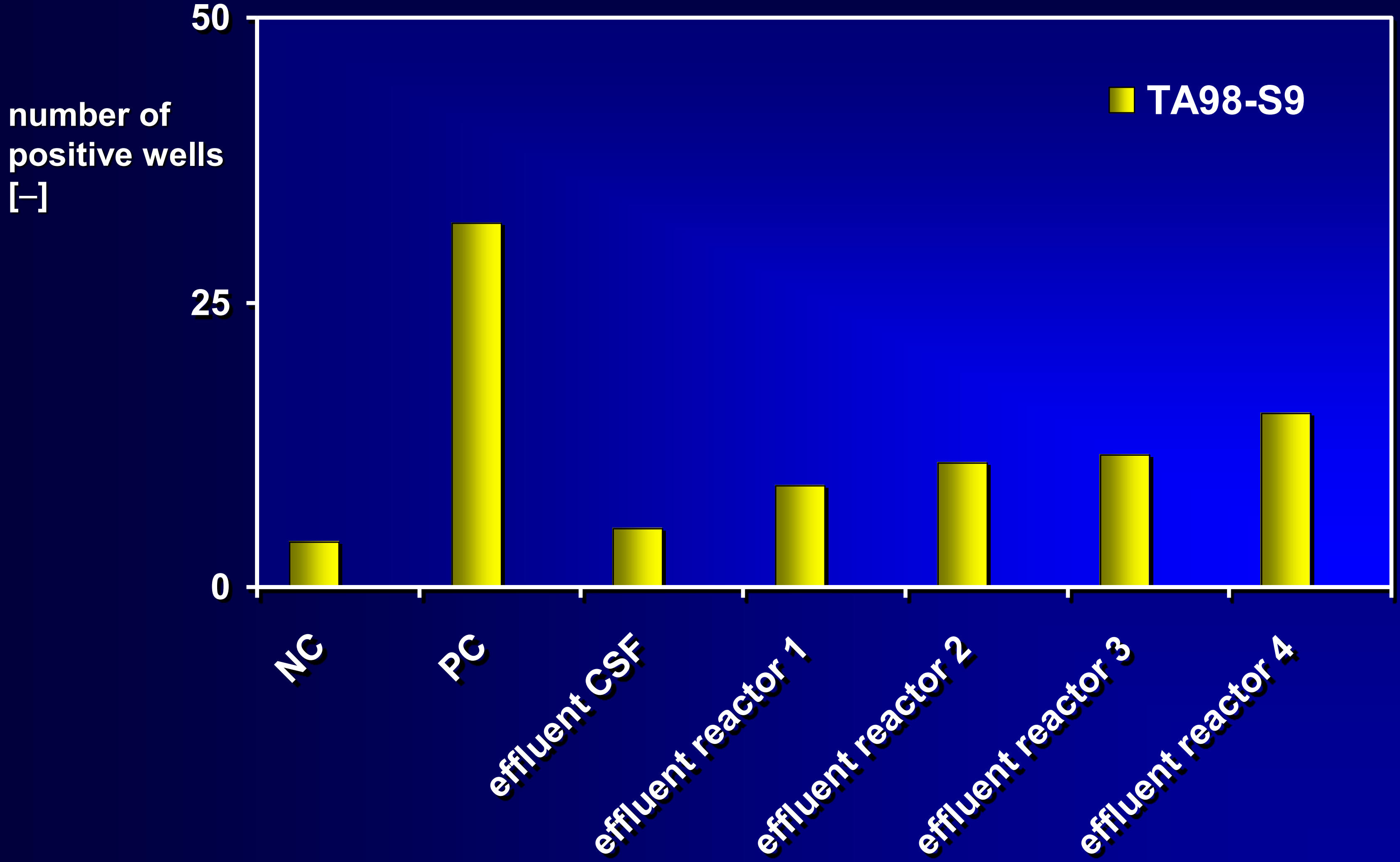
- response in effect measurements
  - *in vitro* in genotoxicity assay Ames II test
  - *in vivo* in fish experiments

in vitro bioassays

- *in vitro* assays
  - measure an effect for instance in cell lines
  - Ames test measuring genotoxicity; DNA damage, mutation in bacterial strain
  - suitable for screening, semi-quantitative

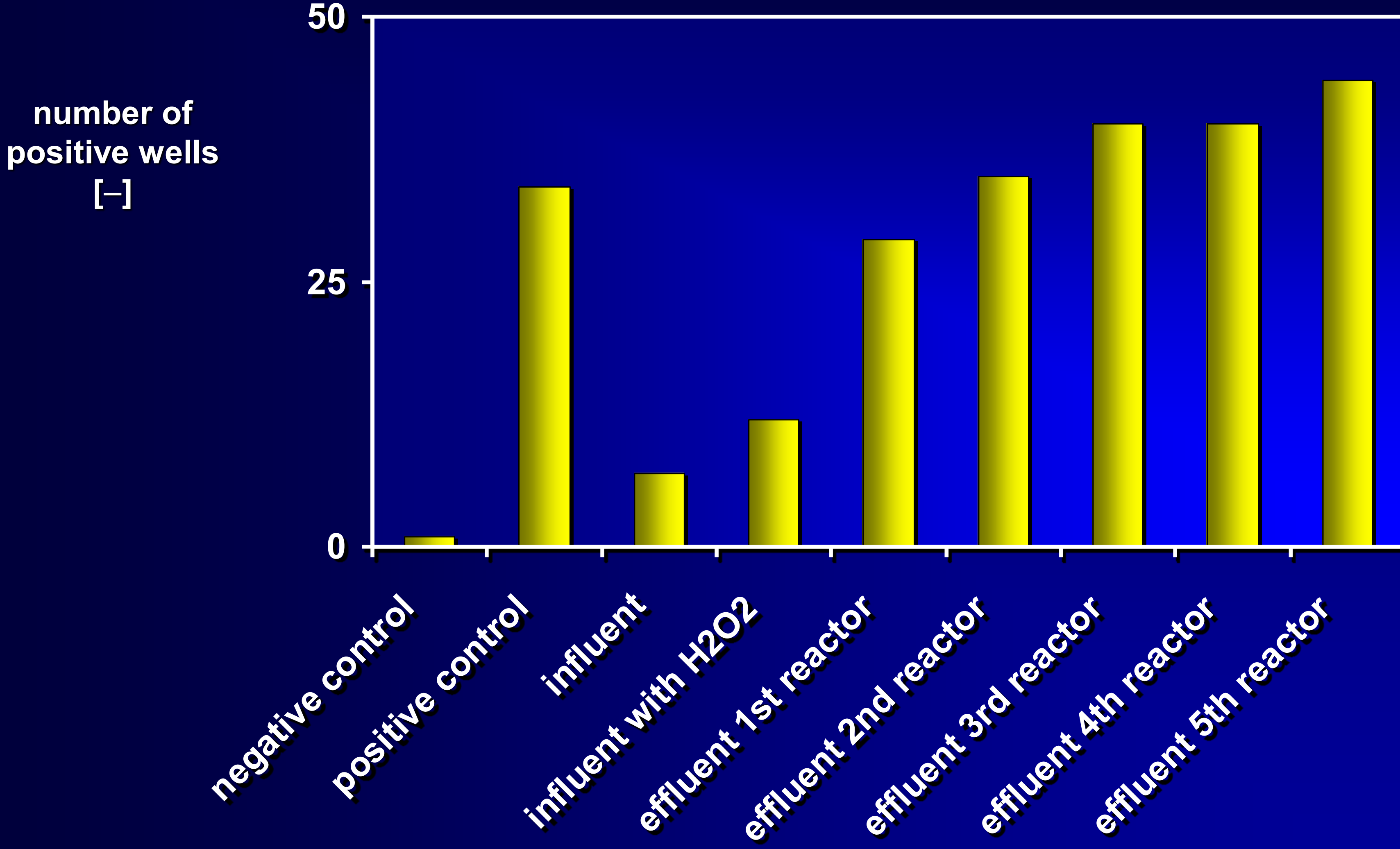
- *in vitro* assay in drinking water treatment requires sample concentration
  - Ames test results: 20,000 concentration factor

Ames test response at wtp Andijk



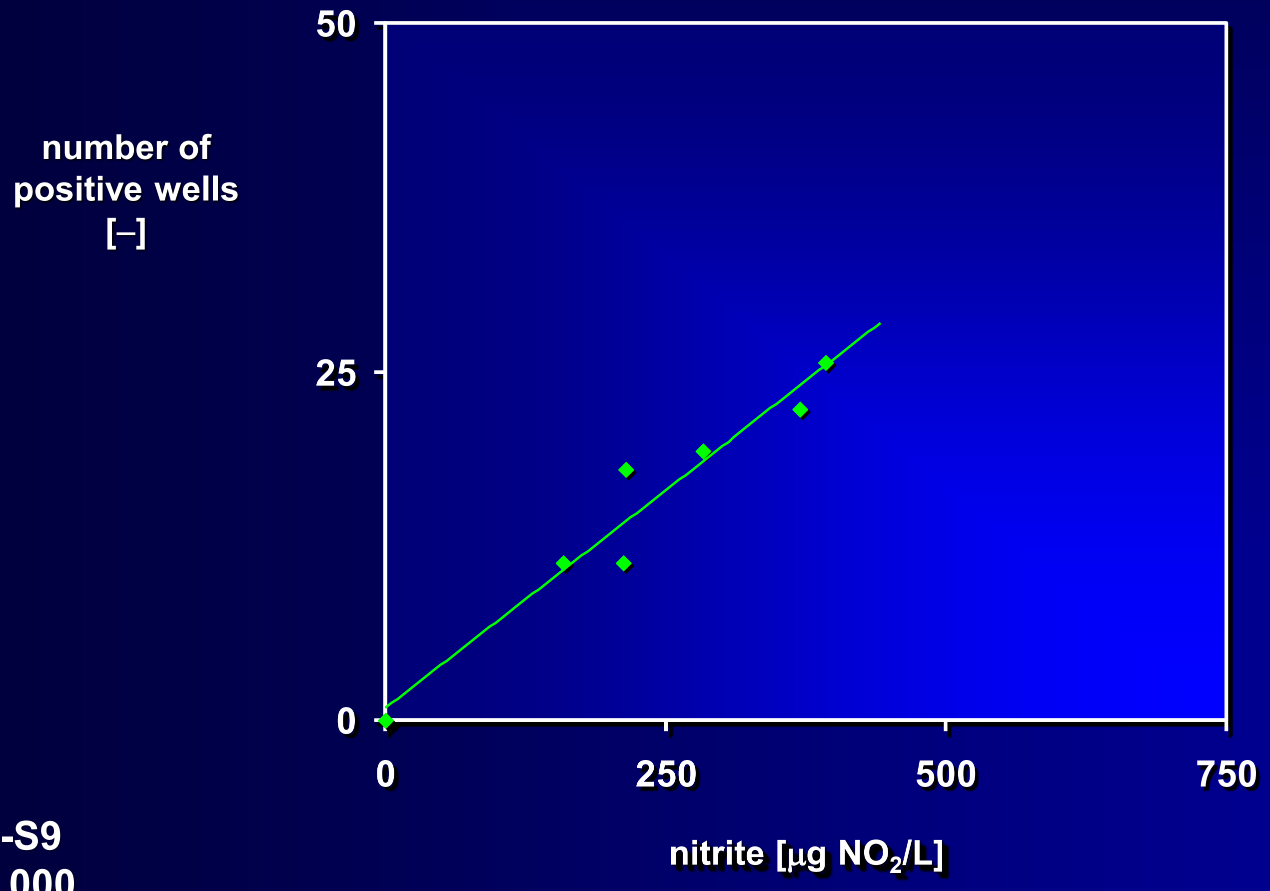
Amestest by VITO laboratory, 2011

Amestest response after MP UV/H_2O_2 treatment at wtp Heemskerk

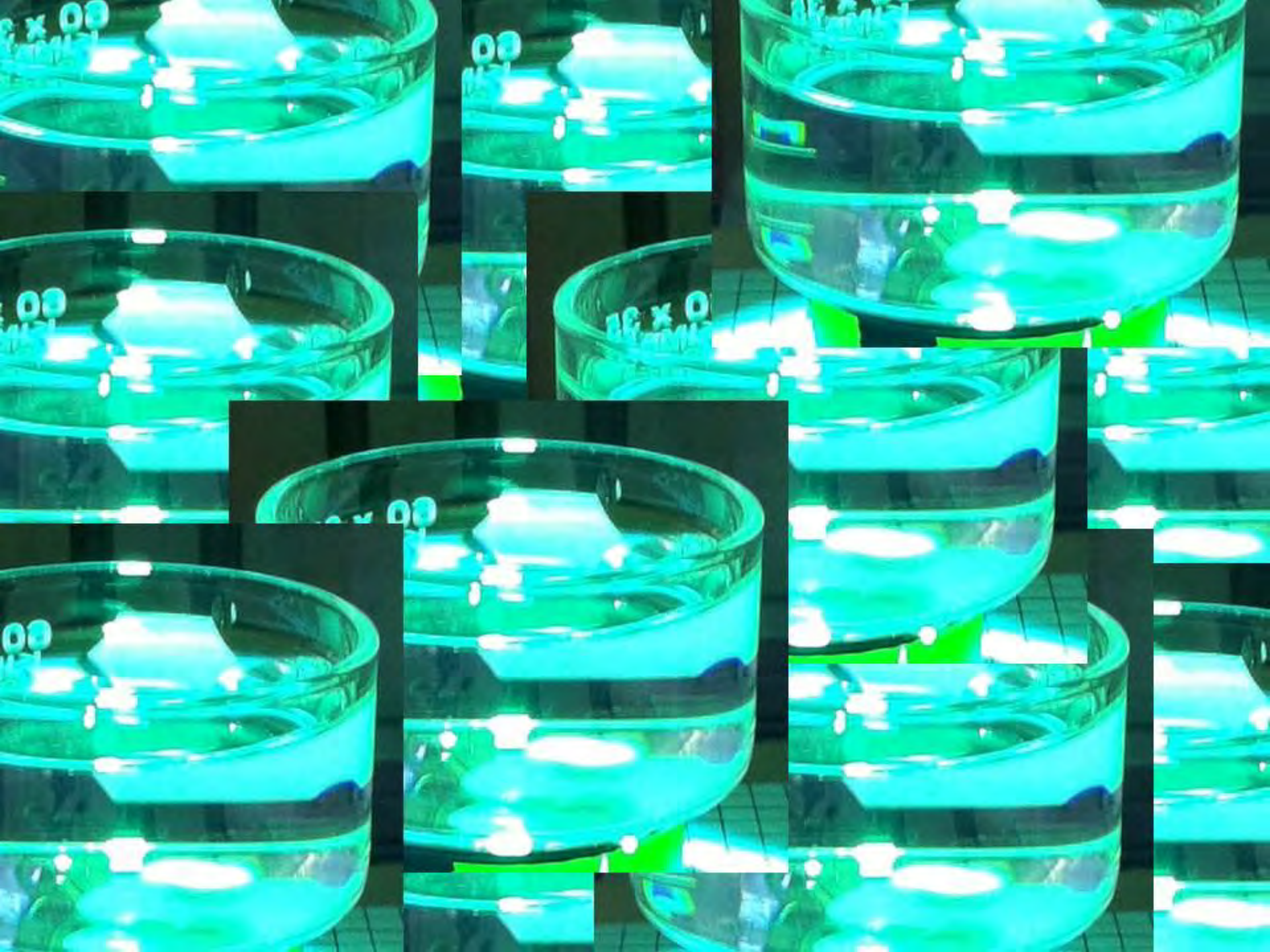


TA98-S9
cf 20,000

relation nitrite formation Amestest response after MP UV/H_2O_2 treatment



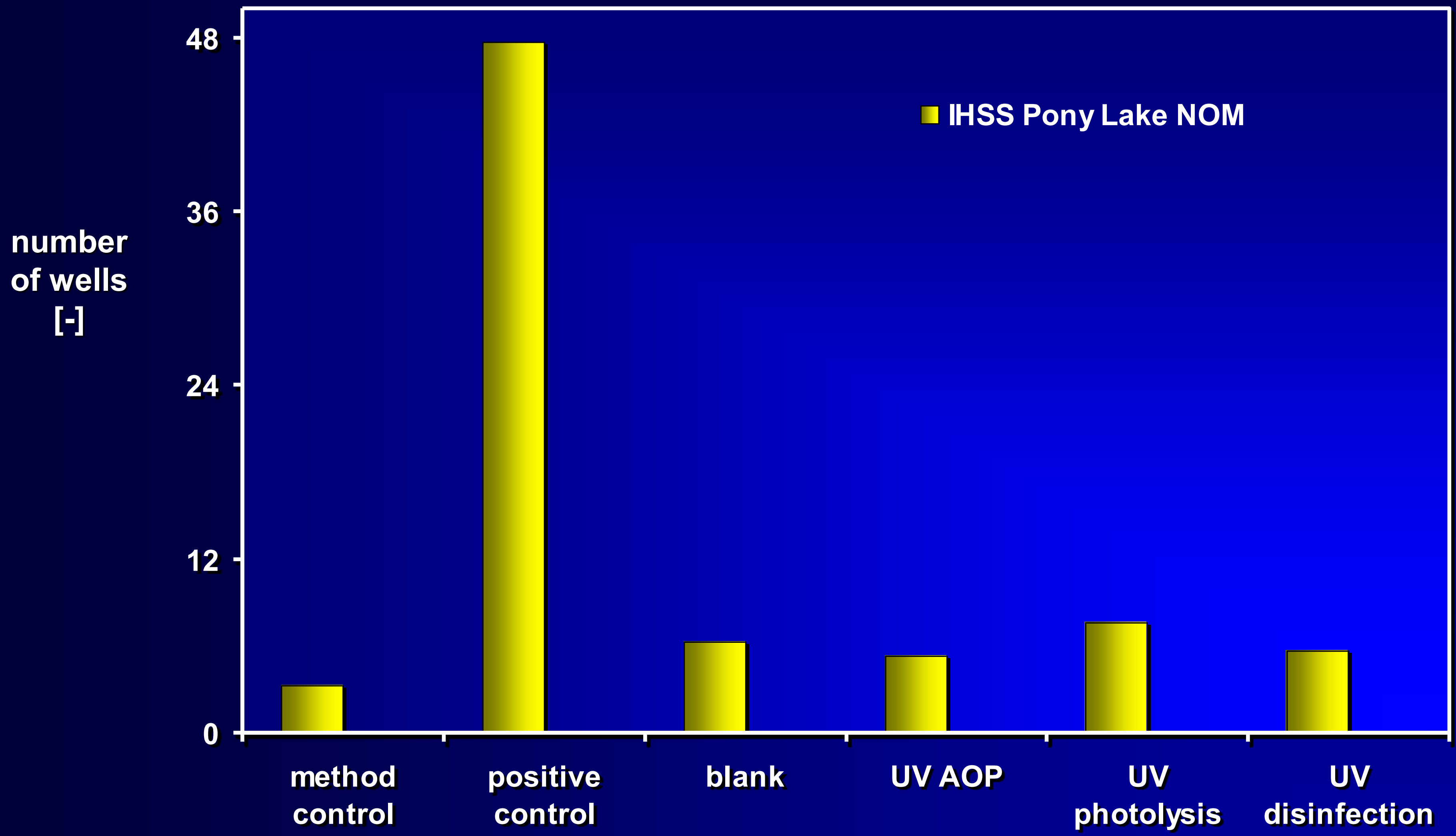
TA98-S9
cf 20,000



bench scale MP UV experiments with reconstituted water

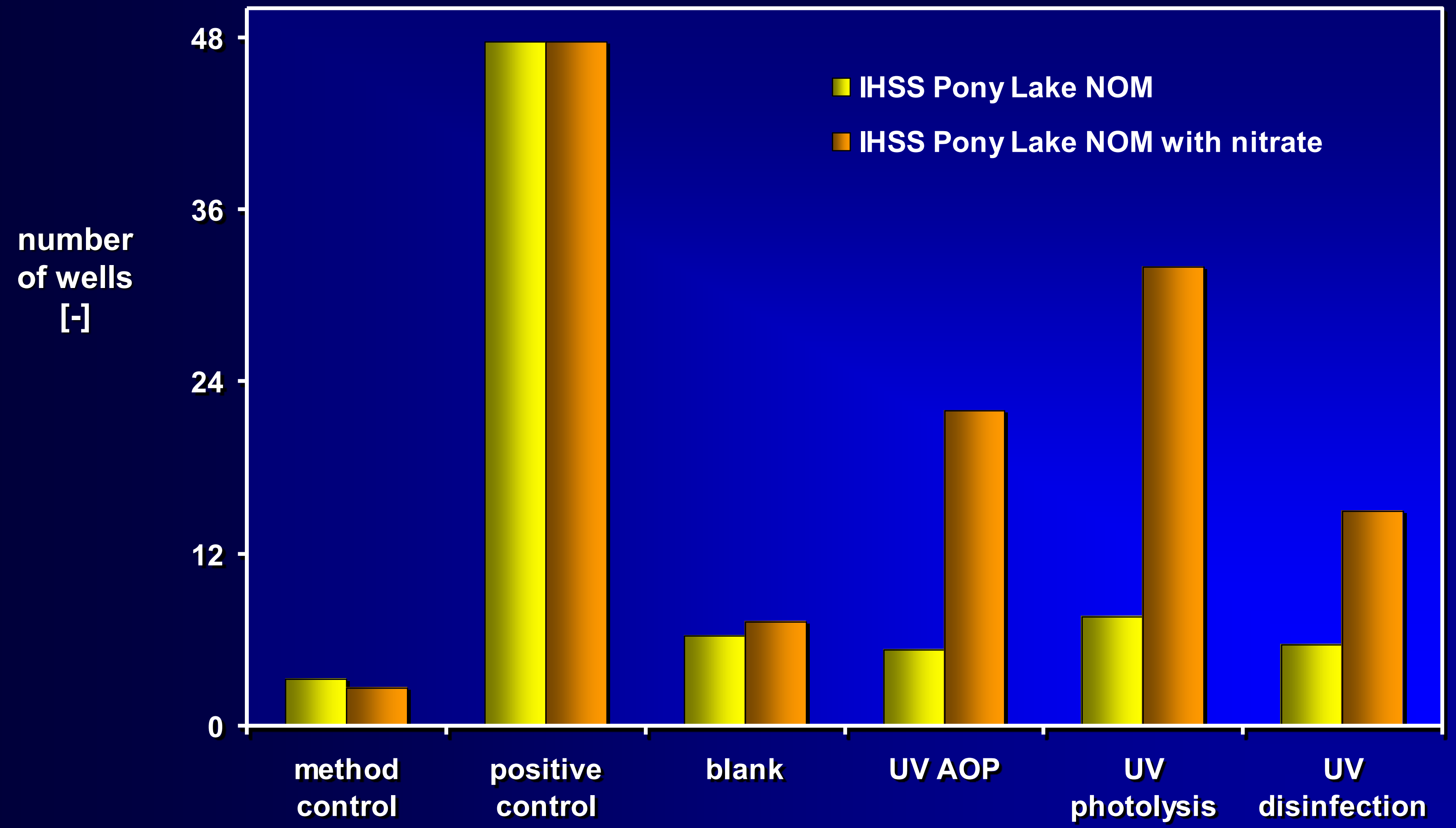
- bench scale MP UV experiments
  - UV-disinfection dose: 40 mJ/cm^2
  - UV/H_2O_2 treatment: 600 mJ/cm^2 icw 6 ppm H_2O_2
- reconsituted water
  - IHSS Pony Lake NOM, 2.5 mg C/L;
  - with and without practical nitrate conc. (10 mg NO_3/L)
- Amestesting and advanced chemical analysis
  - strain TA98-S9 Ames II; SPE OASIS HLB cf up to 20,000
  - N15 labeled nitrate photolysis and orbitrap analysis

Ames response after MP UV/H_2O_2 treatment in reconstituted water



TA98-S9
cf 20,000

Ames response after MP UV/H_2O_2 treatment in reconstituted water



TA98-S9
cf 20,000

MP UV treatment and Ames test

- formation of genotoxic compounds in presence of NOM and nitrate
  - hazard identification
- effect measured
  - no compound(s) identified
  - no concentration established
  - mechanism via nitrate photolysis

chemical identification compounds responsible for Ames test response

- identification required for risk assessment
- hypothesis cause Ames test response
  - aromatic NOM constituents as precursor
  - nitration by nitrate photolysis intermediates
  - multitude of reaction products

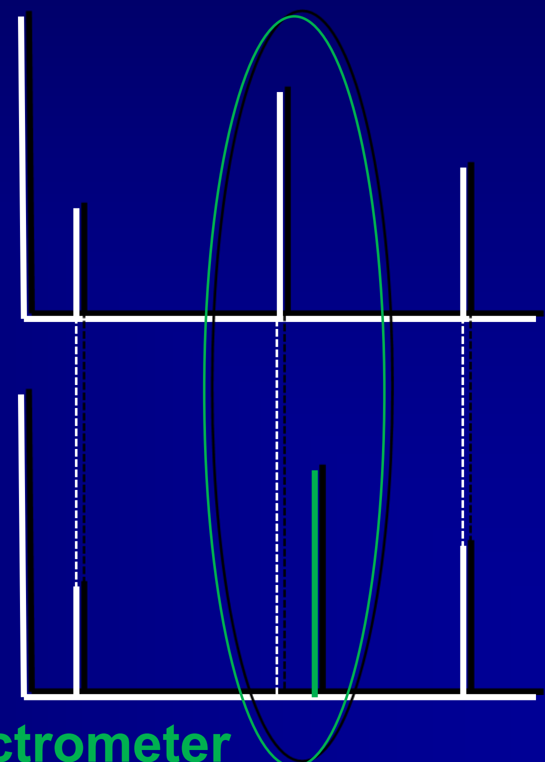
advanced chemical analysis

nitrogen labelling principle

NOM + nitrate (NO_3^-) + MP UV → nitrogen containing byproducts

NOM + nitrate $^{14}NO_3^-$ + MP UV →

NOM + nitrate $^{15}NO_3^-$ + MP UV →



isotope tagging mass spectrometer

results nitrogen labelling

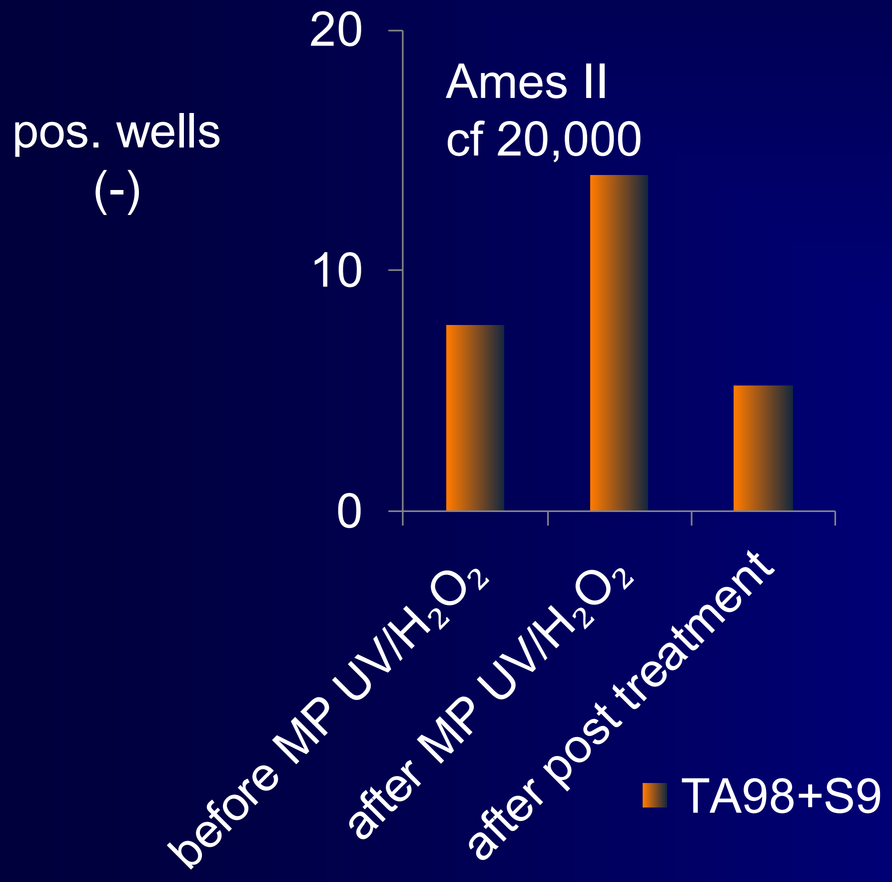
- negative mode orbitrap analysis
  - 78 detected structures
  - 54 different chemical formulas
  - 14 compounds with two ^{15}N atoms
  - total concentration: 1234 ng/L bentazone-d6 eq.

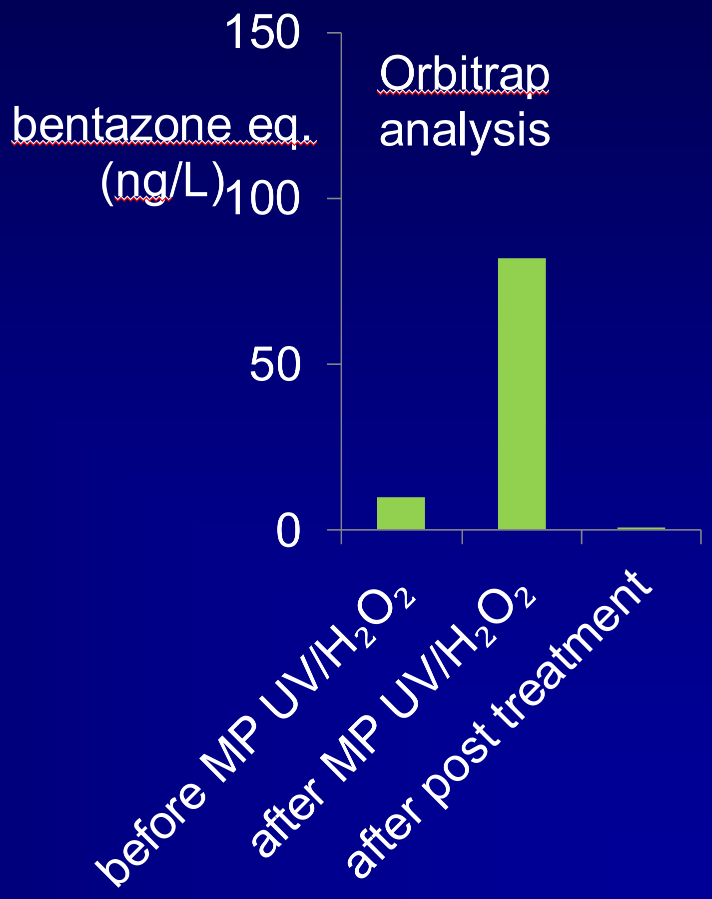
- positive mode orbitrap analysis
  - 16 detected structures
  - 6 different chemical formulas
  - total concentration: 69 ng/L atrazin-d5 eq.

- only few confirmed compounds, none genotoxic

Kolkman *et al. (2015) ES&T,* 49(7) :4458-65

full scale water treatment; bioassay results versus chemical identification





conclusions MP UV reaction product research

- *in vitro* measurements:
  - accumulated effect of a group of related compounds

- labelled nitrogen experiments:
  - identification and quantification of MP UV formed compounds
  - nitrated organic compounds formed by MP UV treatment
  - no genotoxic compound(s) identified by advanced chemical analysis

- state-of-the-art one-compound-one-risk approach most probably not applicable

preliminary risk assessment

- **Toxic Equivalency Factor**
  - **convert Ames test respons in equivalent concentration**
  - **4-NQO as model compound**

- **Margin Of Exposure approach (MOE) for 4-NQO**
  - **ratio between**
    - Bench Mark Dose ($BMDL_{10}$) based on lower limit confidence interval causing 10% tumour incidence
    - Estimated Daily Intake (EDI)

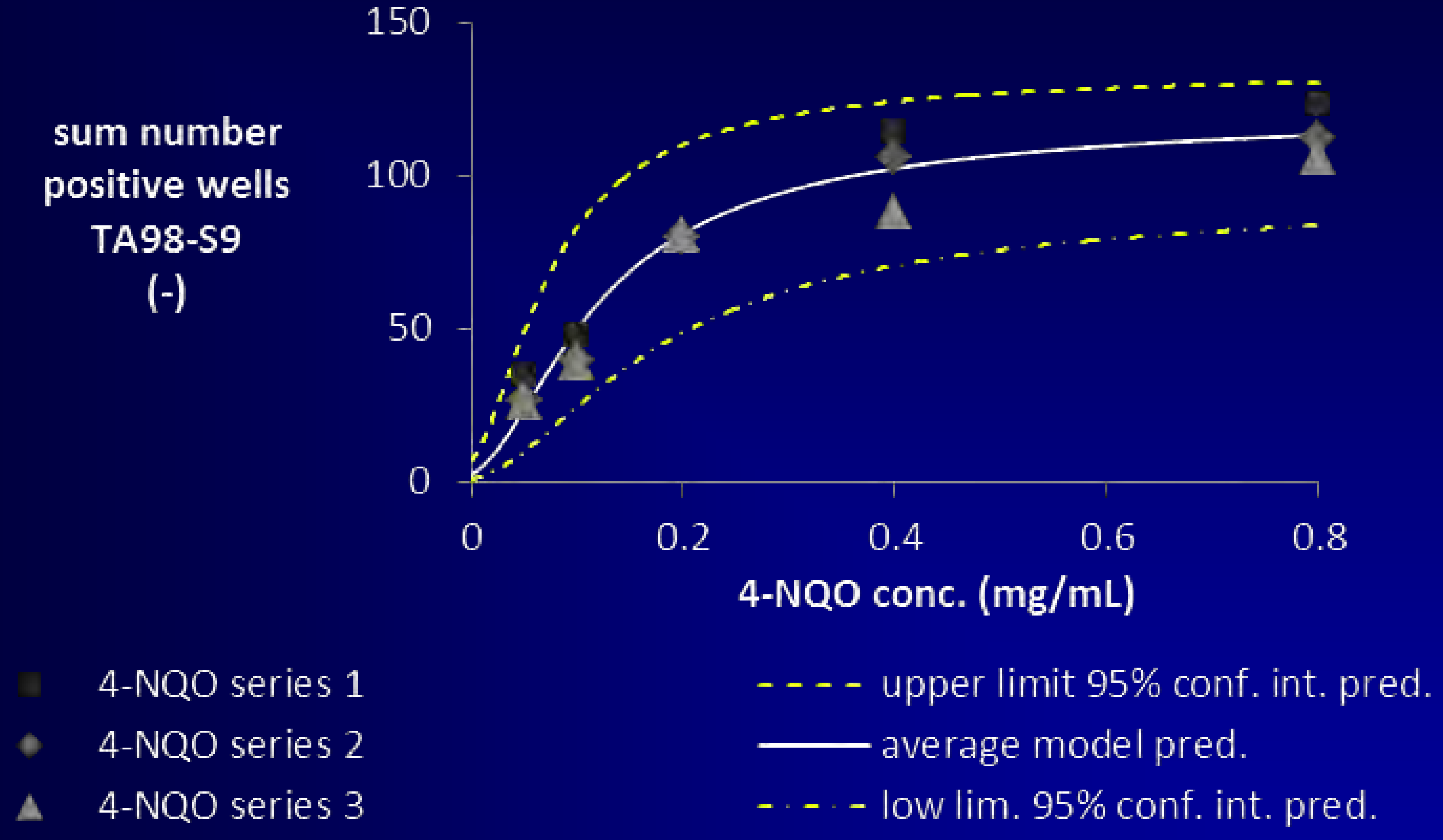
- **MOE > 10,000**
  - **low risk from public health perspective**

4-NQO TEF for MOE > 10,000

- 80 ng 4-NQO eq/L
  - 70 kg body weight
  - 2 liters drinking water per day

- negligible risk when Ames equivalent concentrations < 80 ng 4-NQO eq/L

- determine 4-NQO equivalent dose for observed Ames test results



sum number
positive wells
TA98-S9
(-)
150
100
50
0
0
0.2
0.4
0.6
0.8
4-NQO conc. (mg/mL)
4-NQO series 1
4-NQO series 2
4-NQO series 3
upper limit 95% conf. int. pred.
average model pred.
low lim. 95% conf. int. pred.

TEF based on Ames test respons and conversion into 4-NQO equivalent concentrations

- MP UV AOP on CSF pretreated surface water with nitrate
  - TEF of 300 ng/L 4-NQO observed
- exceeds the level of no concern (80 ng/L 4-NQO)

implications

- application of MP UV treatment of nitrate rich water in the presence of organic matter requires attention in view of side effects

- disclaimer:
  - the used bioassay is only for screening, not to judge actual adverse health effects
  - the 4-NQO tumour data has no mechanistic relationship with the effect of the MP UV induced genotoxic compounds

- biological processes in post treatment by BACF or artificial dunewater recharge remove the formed genotoxic effect and compounds

MP UV/H_2O_2: a reliable barrier for organic contaminant control in an integrated treatment approach

acknowledgements

- KWR Watercycle Research Institute
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- HWL laboratory
- Wetsus
- University of New Hampshire USA

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MOE

- factor 10,000 consists of:
  - factor of 10 for interspecies differences
  - factor of 10 for differences between human individuals
  - factor of 10 for inter individual differences in DNA repair and cell cycle mechanisms
  - factor of 10 for $BMDL_{10}$ was used, and not a ‘no effect’ value

Bench Mark Dose

- tumor data based on 4-NQO and mice
  - 4-NQO was used as starting point
  - 4-NQO was not formed by MP UV, but used as reference
- Based on
  - Tang et al, 2004: 8,000 ng (4-NQO)/kg bw/day
  - US EPA BMD Analysis Framework software

TEF based on Ames test respons and conversion into 4-NQO equivalent concentrations

Practical water matrix	MP UV/H_2O_2 treatment *4-NQO eq. concentration (ng/L)*	MP UV photolysis *4-NQO eq. concentration (ng/L)*	MP UV disinfection *4-NQO eq. concentration (ng/L)*
CSF pretreated surface water	304	>307	221
IX-MF pretreated surface water	135	161	115
aerobic groundwater (low nitrate)	213	211	73
anaerobic groundwater (high nitrate)	196	49	13