

# ESTIMATION OF SAMPLING UNCERTAINTY FOR CONCENTRATION OF ATRAZINE AND DESETHYLATRAZINE IN DRINKING WATER WELLS

Primož Auersperger, Karin Lah  
JP VODOVOD KANALIZACIJA SNAGA d.o.o., Vodovodna cesta 90, Ljubljana, 1000-Slovenia  
primoz.auersperger@vokasnaga.si

## Introduction

Measurement uncertainty of the laboratory analysis is quite well established. However correct estimation of total uncertainty (laboratory + sampling) -  $U_{tot}(k=2)$  for the analytical results is a big challenge, connected also to ISO/IEC 17025:2017 accreditation<sup>2</sup>.

New edition of Eurachem guide<sup>3</sup> about sampling uncertainty discusses new issues connected to correct definition of population where there is an estimation for measurement uncertainty of sampling, evaluation of concentration dependency of uncertainty and many tips for better execution of duplicate method experiments.

We have tested and implemented reasonable cost convenient method for estimation of  $U_{tot}(k=2)$  for concentration of triazine herbicide atrazine (ATR) and its degradation product desethylatrazine (DAT) in waterworks Brest. Parameter value (maximal contaminant level, MCL) from EU Drinking water directive for those contaminants in drinking water is 0,10 µg/L. We followed Eurachem duplicate design and included some other influences on total uncertainty connected with laboratory reproducibility. We used two definitions of population. The first definition is: concentration of ATR (DAT) in pumping well on the day of sampling in case of normal waterworks operation and the second: concentration of ATR (DAT) in pumping well in the week of sampling in case of normal waterworks operation.

For decision rule according to new ILAC-G8<sup>4</sup> edition we used a non-Binary statement with a guard band ( $w=U_{tot}(k=2)$ ).

## Including sampling uncertainty (population A: concentration of ATR (DAT) in pumping well on the day of sampling in case of normal waterworks operation)

In 15 independent sampling campaigns (from November 2016 to August 2019), 56 duplicates were analyzed for ATR and DAT. Concentrations were between 0.0042 µg/L and 0.14 µg/L. First sample was analyzed at the reception and second duplicate sample was analyzed app. after one week, which is the longest storage time. Duplicates for ATR and DAT are evaluated together in order to get different concentration levels. This is possible due to their identical source.

The knowledge about aquifer and operation of waterworks allows exact definition of population including the statement about the normal waterworks operational regime. From pumping tests and concentration changes at operation in waterworks when normal operational regime wasn't present (e.g. some pumping wells were stopped for longer periods) strong influence on concentration of ATR and DAT was discovered. Such situation could be a source of excessive and unpredictable bias for determined concentration of ATR and DAT.

After the comparison of relative (Table 3) and absolute ranges (Table 4) for duplicates (D), approximate concentration area 0.011 µg/L from where relative D could be combined as RMS was chosen. For bias estimation<sup>5</sup> results from Aquacheck trials for triazine herbicides atrazine, simazine, propazine, terbuthryn and prometryn were collected (9 distributions from the year 2016 to the year 2019, in total 46 determinations, Table 1). Five different similar analytes were chosen because main source of bias is connected to uncertainty in purity of the reference materials, which is very similar for a group of triazine herbicides. Uncertainties of reference values were estimated according to ISO 13528:2015. For lower concentration range, biases were estimated from 45 internal QC samples of triazine herbicides and similar compounds at the concentration level 0.006 µg/L (Table 2).

Table 1: Interlaboratory trials, higher concentration range (November 2016 - June 2019).

Parameter	Value	Unit
$N_{results}$	46	-
$u(AV)_{average}$	0.42	%
RMS <sub>bias</sub>	4.09	%
$\mu_{bias}$	4.11	%

Table 3: Duplicates, higher concentration range (April 2018 - August 2019).

Parameter	Value	Unit
$N_{results}$	33	-
$s_{RW}(total)$	3.43	%
$u_{RW}(total)$	3.43	%
$U_{total}(k=2)$	10.71	%

Table 2: Intralaboratory QC, lower concentration range (July 2017 - June 2019).

Parameter	Value	Unit
$N_{results}$	45	-
$u(AV)_{average}$	0.73	%
RMS <sub>bias</sub>	5.70	%
$\mu_{bias}$	0.000345	µg/L

Table 4: Duplicates, lower concentration range (April 2018 - August 2019).

Parameter	Value	Unit
$N_{results}$	16	-
$s_{RW}(total)$	0.000447	µg/L
$u_{RW}(total)$	0.000447	µg/L
$U_{total}(k=2)$	0.001129	µg/L

Proposed model for  $U_{total}(k=2)$ , µg/L:  
 $U_{total}(k=2) = 0.001 + 0.10 * c_x$   
 $c_x$  - concentration of ATR/DAT in sample from 0.0020 µg/L to 0.60 µg/L

## Conclusions

Concentration model of population A for total uncertainty is proposed as:  $U_{tot}(k=2) = 0.001 + 0.10 * c_x$ , where  $c_x$  is concentration of desethylatrazine (atrazine) in concentration range from 0.0020 µg/L to 0.60 µg/L. At MCL 0.10 µg/L  $U_{tot}(k=2)$  is 11.0%. Therefore w is reported at 0.011 µg/L, and parametric value + 0,011 µg/L (0.111 µg/L) for decision rule. We reported results with concentration up to 0.089 µg/L as „pass“, between 0.089 µg/L and 0.100 µg/L as „conditional pass“ between 0.10 µg/L and 0.111 µg/L as „conditional fail“ and results higher than 0.111 as „fail“. Concentration model of population B for total uncertainty is proposed for shallow wells as:  $U_{tot}(k=2) = 0.0003 + 0.20 * c_x$ , where  $c_x$  is concentration of atrazine in concentration range from 0.0020 µg/L to 0.60 µg/L and for deep wells as:  $U_{tot}(k=2) = 0.0004 + 0.12 * c_x$

From described cases, a need for a very precise definition of the population (or sub-population, whatever we defined) is confirmed. In many cases a well-planned combination of laboratory experiments with sampling experiments leads to the most efficient (and cost convenient) estimation of total measurement uncertainty. Only that way in many cases the influence of sampling bias could be avoided.

## Materials

GC-MS Agilent, with auto sampler Gerstel, Switzerland, Silanized injection liners, SGE Australia; Air purifiers, IQAir GCX, INCEN AG, Switzerland; HP SMS UI column, 30 m ID 0,25 mm, df 0,25 µm, Agilent/J&W, USA; Control PC with Chemstation and DRS software Agilent, Alltech SPE vacuum unit for evaporation of 12 samples; Gasses: helium, 99,9999%; nitrogen 99,999% purity, Messer, Slovenia; Dichloromethane HPLC, Acetone HPLC and methanol HPLC Rathburn, Scotland; Pure ATR, DAT, deuterated analogs ATR-D5 and DAT-D6 were from Dr. Ehrenstorfer, Germany.

## Methods

### Sampling

Sampling has been done according to ISO 5667-5:2006 for sampling on faucets. The duplicate samples were collected in time difference up to three hours. At the time of sampling waterworks operated with normal regime.

### SPE GC-MS analysis

Samples were analyzed according to modified EPA 525.2 method. Detailed procedure was published elsewhere<sup>1</sup>. Daily calibration was made with deuterated analogs through the whole procedure including SPE.

## Including sampling uncertainty (population B: concentration of ATR (DAT) in pumping well in the week of sampling in case of normal waterworks operation for deep and shallow wells and additionally for shallow wells in normal meteorological/hydrogeological conditions – stable water levels; excessive positive bias when a water level decreasing and excessive negative bias when a water level increasing)

563 duplicates from February 2011 to July 2019 at different concentration level were analyzed. Excessive deviations connected with a fast water level changes were discarded. First sample was sampled on the first day and second sample of duplicate was sampled app. after one week.

Uncertainty of sampling for deep wells and shallow wells was evaluated separately.

Table 5: Duplicates, shallow wells, higher concentration range (February 2011 - July 2019).

Parameter	Value	Unit
$N_{results}$	100	-
$s_{RW}(total)$	8.99	%
$u_{RW}(total)$	8.99	%
$U_{total}(k=2)$	19.78	%

Table 6: Duplicates, shallow wells, lower concentration range (February 2011 - July 2019).

Parameter	Value	Unit
$N_{results}$	59	-
$s_{RW}(total)$	0.000522	µg/L
$u_{RW}(total)$	0.000522	µg/L
$U_{total}(k=2)$	0.00125	µg/L

Proposed model for  $U_{total}(k=2)$ , µg/L:  
 $U_{total}(k=2) = 0.0003 + 0.20 * c_x$   
 $c_x$  - concentration of ATR/DAT in sample from 0.0020 µg/L to 0.60 µg/L

Table 7: Duplicates, deep wells, higher concentration range (February 2011 - July 2019).

Parameter	Value	Unit
$N_{results}$	268	-
$s_{RW}(total)$	4.12	%
$u_{RW}(total)$	4.12	%
$U_{total}(k=2)$	11.64	%

Table 8: Duplicates, deep wells, lower concentration range (February 2011 - July 2019).

Parameter	Value	Unit
$N_{results}$	133	-
$s_{RW}(total)$	0.000459	µg/L
$u_{RW}(total)$	0.000459	µg/L
$U_{total}(k=2)$	0.00115	µg/L

Proposed model for  $U_{total}(k=2)$ , µg/L:  
 $U_{total}(k=2) = 0.0004 + 0.12 * c_x$   
 $c_x$  - concentration of ATR/DAT in sample from 0.0020 µg/L to 0.60 µg/L

## References

1. P.Auersperger, J.Kus, K.Lah, J. Marsel, High precision procedure for determination of selected herbicides and their degradation products in drinking water by solid-phase extraction and gas chromatography–mass spectrometry, J. Chromatogr. A 2005, 1088, pp 234-241
2. Slovenian accreditation, Measurement uncertainty in sampling and chemical testing, OA-03, Revision 4, in use as of 01-01-2019.
3. Eurachem guide, Measurement uncertainty arising from sampling, 2<sup>nd</sup> edition (2019).
4. ILAC-G8:09/2019, Guidelines on Decision Rules and Statements of Conformity.
5. NT TR 537, 4th edition, Handbook for calculation of measurement uncertainty in environmental laboratories.

## Acknowledgements

This work was financially supported by JAVNO PODJETJE VODOVOD KANALIZACIJA SNAGA d.o.o, Ljubljana which the authors greatly appreciate, especially Kristof Mlakar and Joze Bogolin.

