

BIOMONITORING OF GLYPHOSATE ACROSS THE UNITED STATES IN URINE AND TAP WATER USING HIGH-FIDELITY LC-MS/MS

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Objectives: Glyphosate is the most commonly used pesticide in the world, and its use has rapidly increased since the wide adoption of glyphosate-tolerant crops. While glyphosate is claimed to be safe by its manufacturers, studies over the past decade have reported cytotoxicity, genotoxicity, and endocrine disruption as a result of exposure to glyphosate and glyphosate-containing herbicides. Moreover, the International Agency for Research on Cancer (IARC) conducted its first review of glyphosate in March 2015 and deemed it a Group 2A (Probable) carcinogen. While there have been exposure studies based upon questionnaires, there have been very few biomonitoring studies – due in large part to analytical difficulties in quantifying levels of glyphosate. In the present study we have used LC-MS/MS to measure the levels of glyphosate in tap water and urine samples of volunteer participants from across the United States.

Methods:Urine and tap water samples were prepared using solid phase extraction with Waters WAX column. Analyses were performed using the AB Sciex Triple Quadrupole 5500 mass spectrometer equipped with an Agilent LC1260 set at 4°C. Separations were achieved through a SILIC Obelisc N column (100mm x 2.1mm x 5µm) maintained at 40°C using a mobile phase of 1% formic acid at a flow rate of 1.00mL/min. Glyphosate was monitored using multiple reaction monitoring after electrospray ionization in negative polarity, and quantified by standard addition using an authentic glyphosate reference standard. The method's established limit of quantification is 0.5 ng/mL in urine and 0.01 ng/mL in tap water.

Results: Urine was obtained from 122 individuals from across the United States. Glyphosate was detected in 86.7% of urine samples with an average concentration of 3.0 ng/mL and median of 3.2ng/mL. The highest observed detection frequency was observed in the Midwest (93.3%, mean 3.1ng/mL) while the lowest was observed in the South (69.2%, meana 2.6ng/mL).

Of the 52 water samples screened, only two samples from the West Coast have detectable glyphosate levels at 0.017 and 0.023 ng/mL.

Conclusions: Although glyphosate was only detected in two of 52 tap water samples, it was detected in the majority of urine samples analyzed. The current study is both the largest biomonitoring study of glyphosate in urine and utilizes the most sensitive urine LC-MS/MS method published to date. The high detection frequency of glyphosate in urine adds to the growing evidence that larger biomonitoring studies of glyphosate in the general population is warranted.