Multiresidue method for the determination of pesticides in odonate nymphs as ecosystem biomonitors
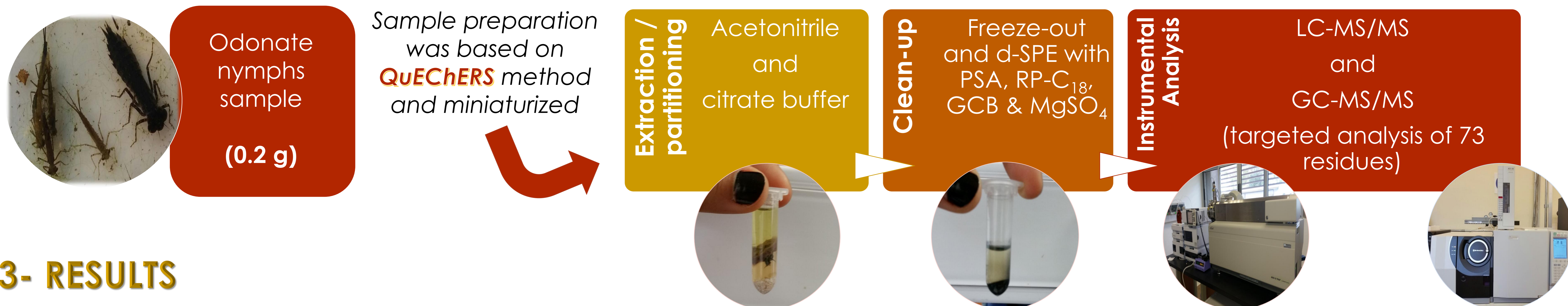
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1- INTRODUCTION

Aquatic macroinvertebrates are frequently used as bioindicators of water quality due to their relationship with land use. Odonate nymphs, which belong to the functional group of predators, were selected for the present study aiming to evaluate their pesticides bioaccumulation potential and their ability to biomonitor the environments. The first step to achieve these goals was to develop and validate an analytical method for the extraction and determination of pesticides in them. A QuEChERS[1] sample preparation strategy was adapted. The studied aquatic macroinvertebrates are small organisms which are difficult to find and collect in large amounts, especially in disturbed ecosystems. Therefore, the method was modified in order to analyze small sample amounts using minimal extraction solvent volumes. The adjustment and validation of an expanded scope QuEChERS based methodology using LC-MS/MS and GC-MS/MS as instrumental detection systems for a total number of 46 LC plus 27 GC amenable pesticides is presented.
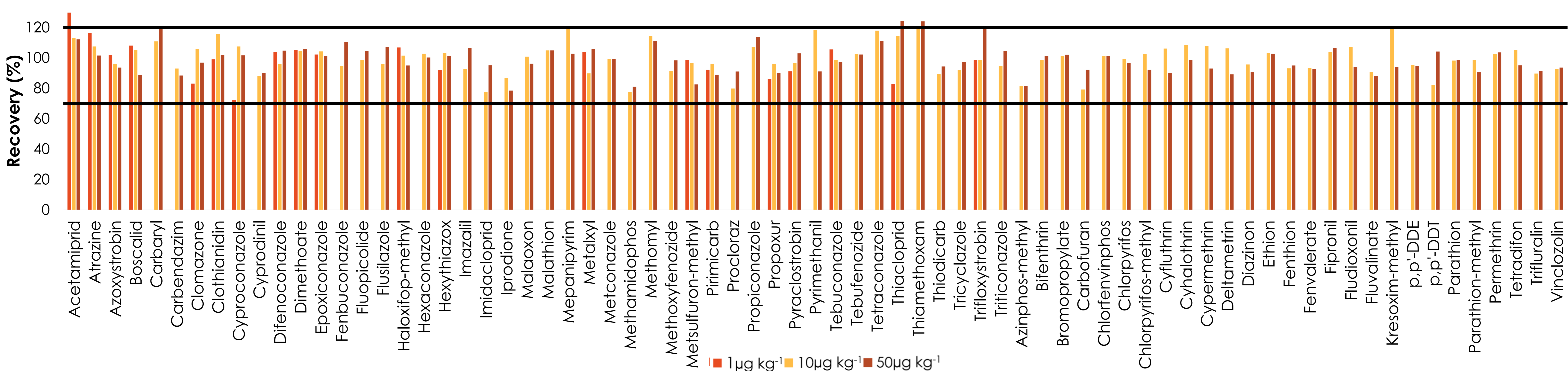
2- EXPERIMENTAL

Odonate nymphs sample **(0.2 g)** → Sample preparation was based on **QuEChERS** method and miniaturized →

Extraction / partitioning	Clean-up	Instrumental Analysis
Acetonitrile and citrate buffer	Freeze-out and d-SPE with PSA, RP-C$_{18}$, GCB & MgSO$_4$	LC-MS/MS and GC-MS/MS (targeted analysis of 73 residues)

3- RESULTS

3.1- Method validation (following DG-SANTE[2] guidelines)

Recoveries of the pesticides at the three assayed levels (1, 10 and 50 µg kg^{-1}) with RSDs below 20%:

Recovery (%) bar chart for pesticides: Acetamiprid, Atrazine, Azoxystrobin, Boscalid, Carbaryl, Carbendazim, Clomazone, Clothianidin, Cyproconazole, Cyprodinil, Difenoconazole, Dimethoate, Epoxiconazole, Fenbuconazole, Fluopicolide, Flusilazole, Haloxifop-methyl, Hexaconazole, Hexythiazox, Imazalil, Imidacloprid, Iprodione, Malaoxon, Malathion, Mepanipyrim, Metalxyl, Metconazole, Methamidophos, Methomyl, Methoxyfenozide, Metsulfuron-methyl, Pirimicarb, Procloraz, Propiconazole, Propoxur, Pyraclostrobin, Pyrimethanil, Tebuconazole, Tebufenozide, Tetraconazole, Thiacloprid, Thiamethoxam, Thiodicarb, Tricyclazole, Trifloxystrobin, Triticonazole, Azinphos-methyl, Bifenthrin, Bromopropylate, Carbofuran, Chlorfenvinphos, Chlorpyrifos, Chlorpyrifos-methyl, Cyfluthrin, Cyhalothrin, Cypermethrin, Deltametrin, Diazinon, Ethion, Fenthion, Fenvalerate, Fipronil, Fludioxonil, Fluvalinate, Kresoxim-methyl, p,p'-DDE, p,p'-DDT, Parathion, Parathion-methyl, Permethrin, Tetradifon, Trifluralin, Vinclozolin. Legend: ■ 1 µg kg^{-1} ■ 10 µg kg^{-1} ■ 50 µg kg^{-1}

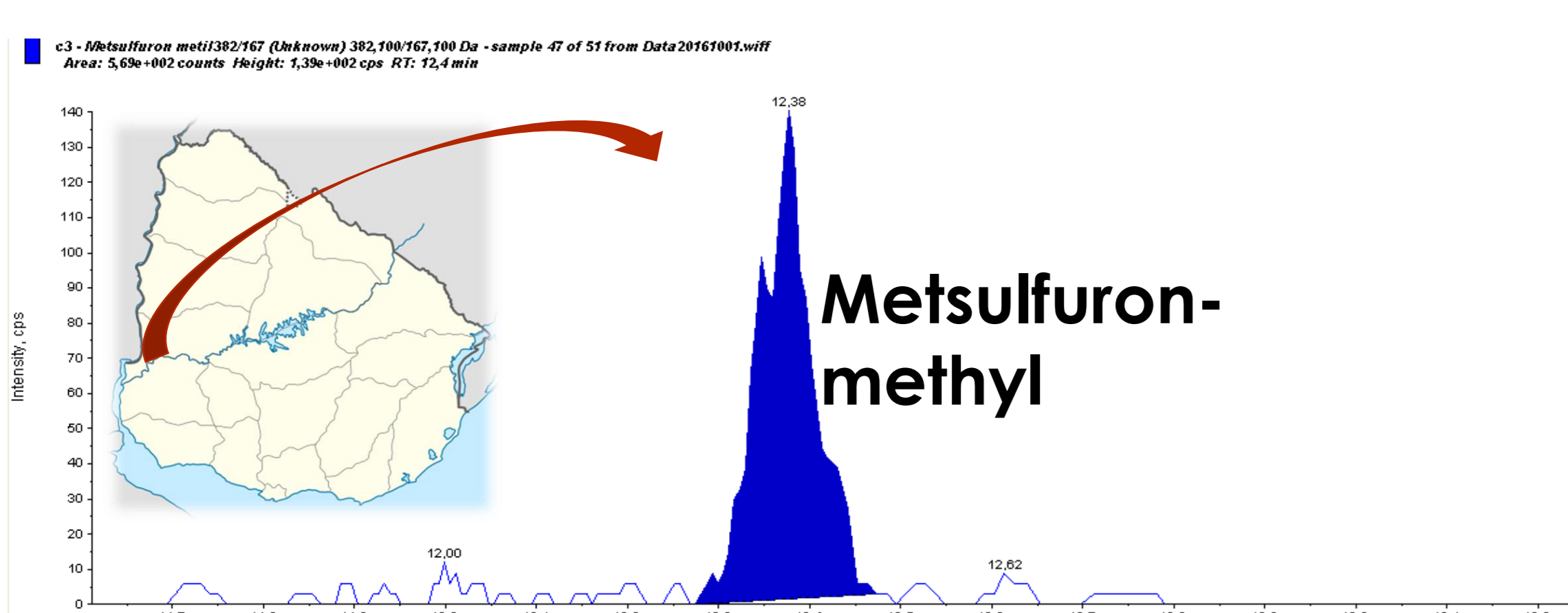| Trueness	Precision	Matrix effect	Linearity	LOQs
Recoveries were between 72 – 120% (at least 2 assayed levels)	RSDs were ≤ 20% for all the analytes at all assayed levels	For 98% of LC amenable pesticides, matrix effect was null	Linear ranges: • 1-100 µg kg^{-1} • 10-100 µg kg^{-1}	1 µg kg^{-1} for 19 analytes and 10 µg kg^{-1} for the others

3.2- Real samples analysis

Positive finding of metsulfuron-methyl at 1 µg kg^{-1} in a sample of odonate nymphs from the Río Negro, Uruguay

4- DISCUSSION & CONCLUSIONS

- It was possible to develop and validate an analytical methodology for the determination of 73 pesticides in odonate nymphs by LC-MS/MS and GC-MS/MS.

- The analytical methodology was developed taking into account the particular characteristics of the assayed matrix, fitting for purpose.

- The adapted QuEChERS strategy uses minimal amounts of reagents and produces less waste, which makes it environmentally friendly.

- This methodology is suitable for real samples analysis, aiming to contribute to the monitoring of the ecological state of fresh water and a useful tool to complement ecotoxicological observations based on odonates occurrence.

5- REFERENCES
1- Anastassiades, M et al. 2007. In: Ohkawa H, Miyagawa H, Lee PW. [Eds.]. Pesticide Chemistry: Crop Protection, Public Health, Environmental Safety. Weinheim: Wiley-VCH. pp. 439-458.
2- European commission directorate-general for health and food safety. SANTE/11945/2015.