## BIOMONITORING LONG AND SHORT TERM EXPOSURE TO PENCONAZOLE USING HAIR AND URINE SPECIMENTS

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**Background:** Penconazole (PEN) is a fungicide widely used in vineyards.

**Aim of the study:** To identify urinary metabolites for biological monitoring of occupational exposure to PEN; to assess the suitability of hair as a matrix of long-term exposure to PEN.

**Methods:** Winegrowers (16 subjects) exposed to PEN collected cumulative urine sample respectively for: 24 h before the first application (Pre-WS), during the application (WS1, WS2, and WS3), after the application since the next work shift (Post 24h 1 and Post 24h 2), the last work day for 24h after the application (Last post 24h), and a last sample from 25th to 48th hour after the application (Post 25-48h). Urine samples were analyzed by LC-MS/MS to obtain a profile of candidate metabolites. Based on the presence of the triazole moiety in the full scan mass spectra major candidates were found. From their mass spectra hydroxy and carboxy-penconazole (PEN-OH and PEN-COOH), both as free molecules and as glucuronide conjugates, were identified. The free molecules were quantified in urine samples after hydrolysis. Hair samples of 13 winegrowers, 3 family members of winegrowers, and 5 technicians involved in samples collection were collected before and after the treatment season (samples PRE- and POST-EXP). PEN in hair was desorbed with acetonitrile and extracts were analyzed by LC-MS/MS.

**Results:** PEN-OH was the most abundant metabolite with a wide inter-subject variability. Mean PEN-OH and PEN-COOH levels were in the 1.3-237.0 μg/L and 0.5-54.1 μg/L ranges, respectively. Excretion of PEN metabolites increased with consecutive work shifts. Urinary metabolites were correlated with the potential and actual dermal exposure assessed measuring PEN on the work clothes and on the skin, with Pearson r up to 0.428 in Post 25-48h samples. In hair samples, PEN was quantifiable in most PRE-EXP samples (0.010 ng/mg hair) and in all POST-EXP samples (0.060 ng/mg hair) with a significant increase ($p=0.005$). PEN was quantifiable in all POST-EXP families (0.011 ng/mg hair) and technicians (0.005 ng/mg hair); in winegrowers it was higher than the other two groups ($p=0.022$).

**Conclusions:** The results obtained suggest that PEN-OH in post-exposure urine sample and hair PEN are promising candidate for biomonitoring short- and long-term exposure to PEN in agriculture workers.