Fate of glyphosate and AMPA in the vadose zone: dissipation, transport and adsorption

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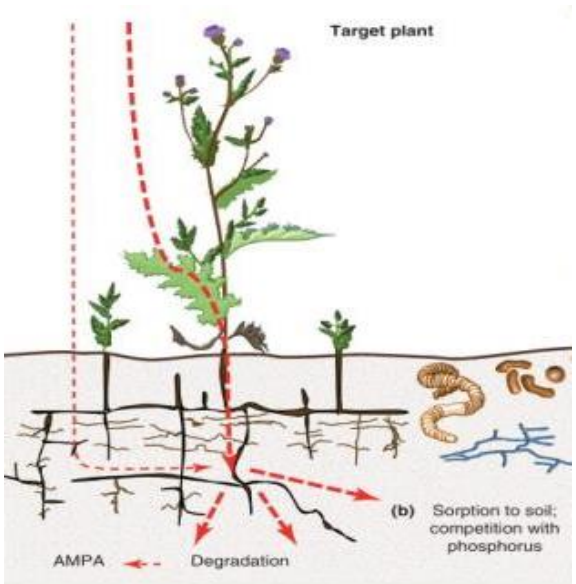
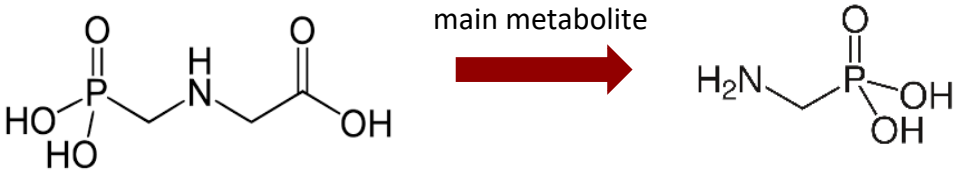
EGU2020: Sharing Geoscience Online, May 2020

Glyphosate (GLP): the herbicide

- One of the most applied herbicide worldwide;
- Post-emergence application, foliar adsorption, sistemic and non-selective;
- Inhibition of the plant enzyme 5-enolpyruvylshikimate-3-phosphate synthase, blocking the production of three essential aminoacids;
- IARC (2015): Potentially carcinogenic; EFSA (2015): not likely carcinogenic.
- **The EU limit for drinking water is 0.1 µg L^{-1}**





GLP **AMPA**

The Prosecco Production Area

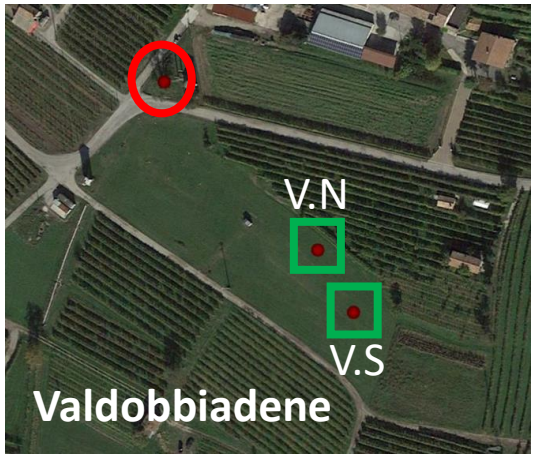
- Widely extensive vineyard area for the production of Prosecco DOCG.
- Recently included in the UNESCO's World Heritage List.
- GLP has been extensively applied.
- Site-specific studies around catchment wells for drinking water are required to identify protection areas.

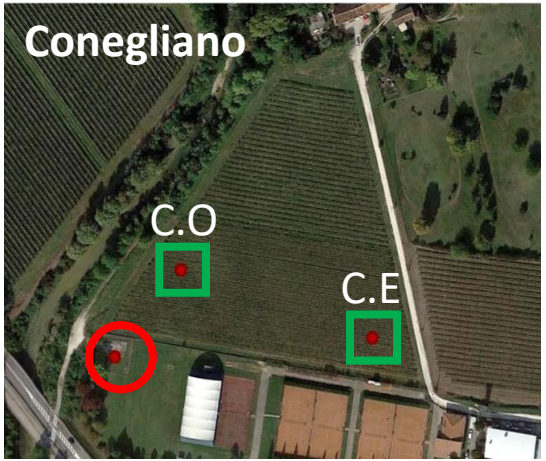
Aim of the research

1. To understand glyphosate-AMPA dissipation-adsorption dynamic in soils in the Prosecco wine production area;
2. To find which soil properties affects more GLP adsorption;
3. To Identify most vulnerable areas to GLP contamination of soils and aquifers.

Experimental Design

Two Experimental sites within the Prosecco area production





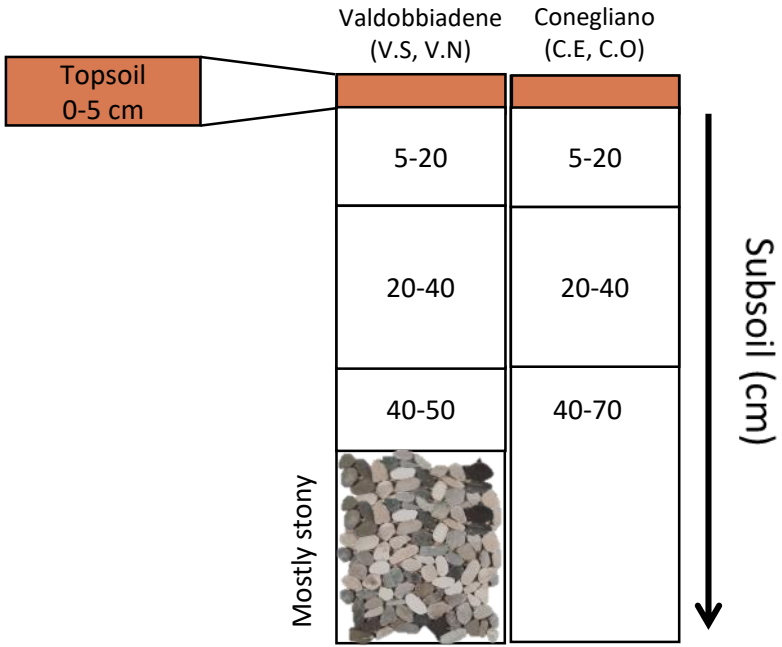
Each site was equipped with:

- **One weather station**
- **Two soil-water monitoring stations (Valdobbiadene: V.N and V.S; Conegliano: C.O and C.E)**

at 10, 30, 70 cm → suction cups, soil temperature and volumetric water content probes.

Each plot (25 m^2) was treated with a 4.94 g L^{-1} GLP solution on November 2018 on uncontaminated soil.

Sampling Design



Soil physical and hydraulic characterization

Undisturbed soil cores along the profile (down to 70 cm) were collected and analysed for hydraulic, physical and chemical properties.

Monitoring of GLP and AMPA on water and soil

→Soil-water samples were collected for 6 months (November 2018 – May 2019) at each depth;

→Soil samples were collected from November 2018 until September 2019 at different soil depth (*topsoil* 0-5 cm and *subsoil* 5-20, 20-40, 40-50 cm -Valdobbiadene- and 40-70 cm -Conegliano).

Both GLP and AMPA in water and soil were analysed on HPLC-MS *(Carretta et al., 2019)*

Dissipation and Adsorption study

Dissipation

Dissipation dynamic of GLP was monitored applying the SFO (single first-order) kinetic model:

$$C_t = C_0 e^{-kt}$$

C_t → GLP concentration at the time t (μg kg^{-1})
C_0 → initial GLP concentration (μg kg^{-1})
k → dissipation coefficient
t → time (days)

Adsorption

Five concentrations of GLP in the range of 0.1-25 μg g^{-1} of dry soil were tested applying the *OECD Guideline* using the Batch Equilibrium Method. Adsoprtion study was performed all along the soil profile for the three different soil layers.

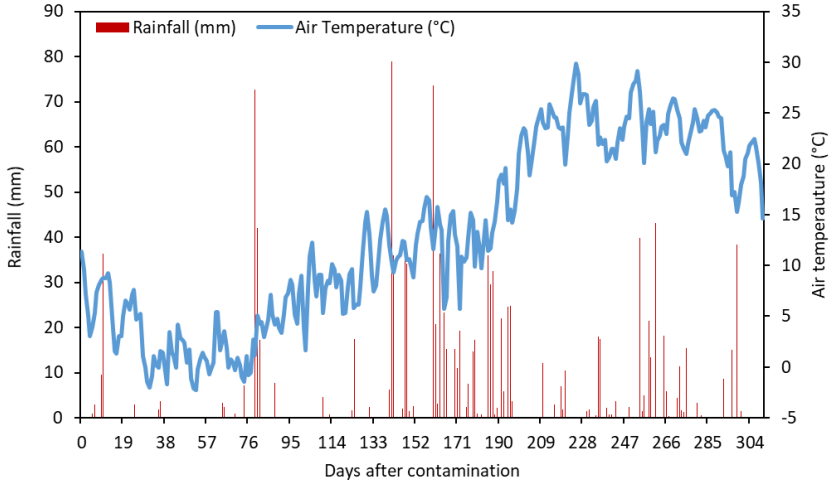
The Freundlich adsorption isotherm was used to fit GLP adsorption data:

$$Q_e = K_f C_e^{(1/n)}$$

Q_e → amount of sorbed GLP to soil particles (μg g^{-1})
K_f → Freundlich adsorption coefficient ((μg$^{1-1/n}$ (mL)$^{1/n}$ g^{-1})
C_e → GLP concentration in water (μg mL^{-1})
n → regression constant

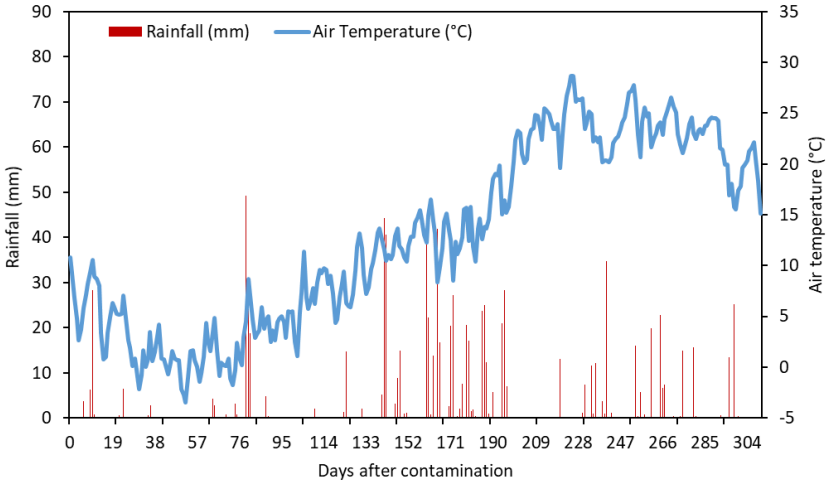
Meteorological conditions

Valdobbiadene



Cumulated rainfall: 1216.8 mm

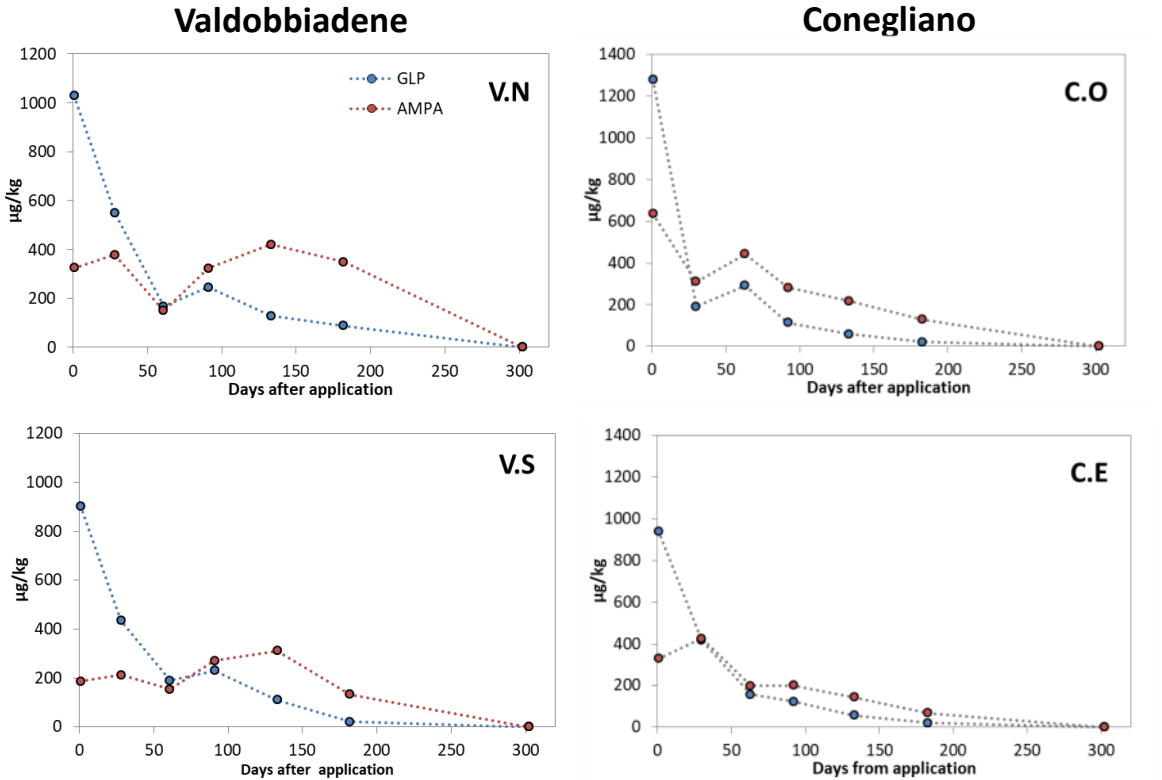
Conegliano



Cumulated rainfall: 905.6 mm

Valdobbiadene showed strongest rainfall events, while the air temperature was similar between the two sites although +0.18 °C on average was recorded.

GLP decay and AMPA formation in *topsoil*



- Plots within the same site showed a similar trend on GLP–AMPA dynamic.
- C.O and C.E showed faster GLP-AMPA dissipation/formation.
- AMPA formation was slower in V.N and V.S than C.O and C.E.
- Max concentrations of AMPA were at 120 days in V.N and V.S., at 30 days in C.E and C.O.

GLP decay and AMPA formation in *subsoil*

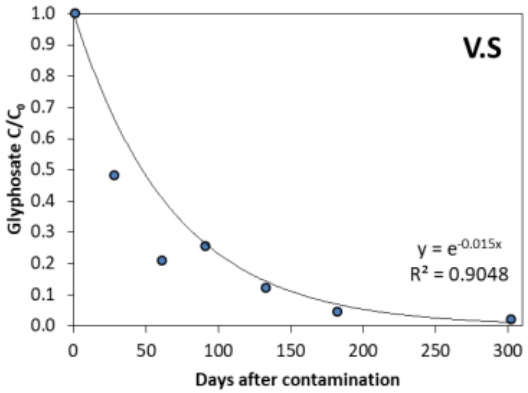
Site	V.N	V.S	C.O	C.E		
Depth (cm)	40-50	40-50	5-20	5-20		40-70
Day	91	133	1	1	92	92
GLP (µg/kg)	80.7	63.1	308.8	80.4	45.6	53.8
AMPA (µg/kg)	64.6	-	72	-	-	-

Strong rainfall event on 01/02/2019
Valdobbiadene: 72.8 mm
Conegliano: 49.6 mm

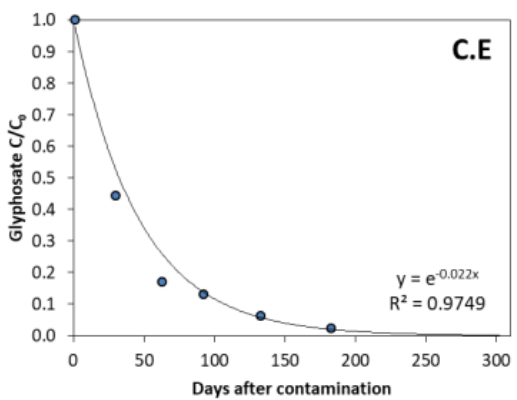
- GLP and AMPA were seldom detected in the subsoil but with high concentrations → possible risk.
- Both V.N and V.S showed higher leaching potential of GLP and AMPA → they were found even in the deepest layer after strong rainfall events.
- GLP in Conegliano → mostly adsorbed in the shallow layer (5-20 cm).
- AMPA → in V.N after 91 days and in C.O the day after contamination (day 1). In V.S and C.E was never detected.

GLP Dissipation (DT_{50})

Valdobbiadene



Conegliano



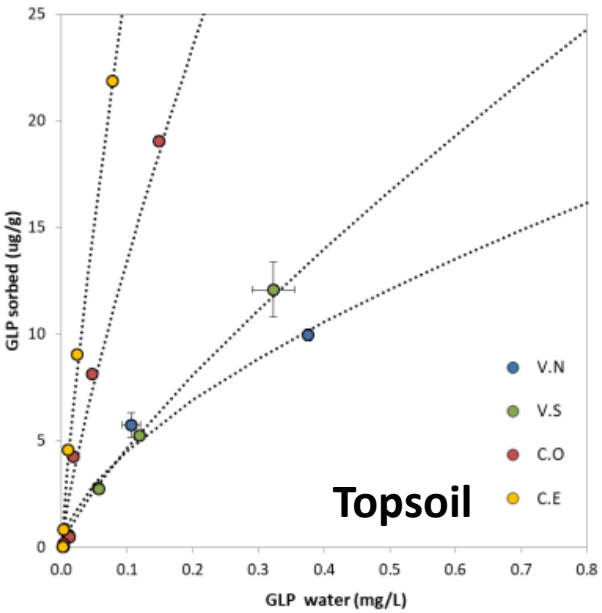
***Topsoil* layer: 0-5 cm**

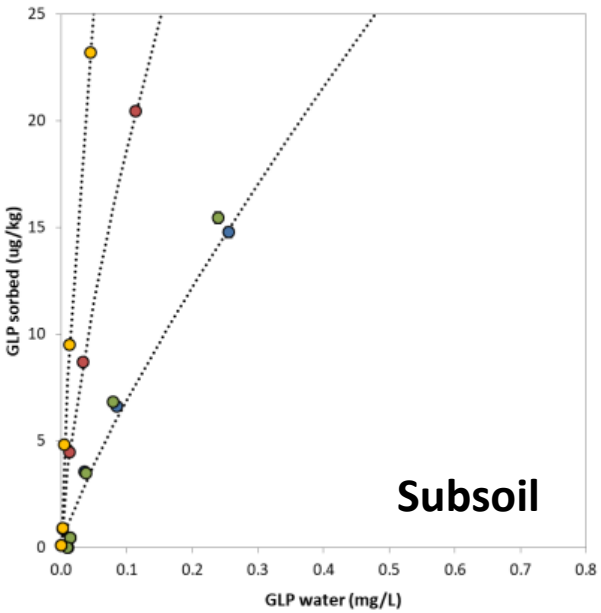
GLP in Conegliano site showed faster dissipation decay than Valdobbiadene:
higher soil microbial activity and GLP degradation?

Site	GLP (g m^{-2})	k	DT_{50} (days)	C/N
Valdobbiadene	0.168	0.015	47.85	8.55
Conegliano	0.208	0.023	30.20	7.89

Average values

GLP Adsorption





Full soil Profile

- Conegliano showed the highest GLP adsorption compared to Valdobbiadene.
- GLP exhibited the higher adsorption in the deepest layer.

GLP adsoprtion coefficient (K_f) was correlated with some soil properties: texture (*sand*: R=-0.91 and *clay*: R=0.72) and *cation exchange capacity* (CEC: R=0.81).

Conclusion

- GLP followed a first order dissipation dynamic in all monitoring stations;
- AMPA persisted more than GLP. However both molecules were not detected at the end of the sampling period for both experimental sites (302 days);
- DT_{50} was lower for Conegliano than Valdobbiadene attesting a faster GLP degradation
- GLP adsorption followed Freundlich isotherm. GLP was found to be strongly sorbed in Conegliano soil and in the subsoil layer rather than the topsoil.
- Future research:
  → Modelling of GLP and AMPA dynamics in the long-term
  → Linking GLP and AMPA dynamics between soil and groundwater

Thank you for your attention

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Acknowledgments:
Uni-Impresa Grant through the project "SWAT"
(University of Padova)
Altro trevigiano Servizi Srl
Piave Servizi Srl