Copper accumulation in vineyards soils of Lombardy and its transfer to surface and ground water - A survey in *Oltrepò pavese.*

V.M. SALE[Δ], M.L.GARGANO[Δ], S. BRENNA[Δ], A. LEONI[Δ], E. SACCHI[*], S. FORNELLI GENOT[*]

[Δ] *ERSAF, via Taramelli 12, 20125 Milano, +3902 67404653*

[*] Universita di Pavia, *Via Ferrata 1, 27100 Pavia, +390382 985880*

Introduction

Copper (Cu) contained in pesticides causes in Italian vineyards soils concentrations from 400 to 600 ppm, much higher than those allowed in soils intended for residential or parks and gardens use (120 ppm). The soil layer affected by Cu accumulation is about 50 cm thick, the maximum of concentration lies in the top and decreases with depth. In the hilly soils erosion can lead to the transport into streams of residual Cu distributed to grapes with pesticides. The average of Cu concentration observed in the ground water (3-5 ppb) is largely below the limit established by OMS and the Italian law on drinking water (1ppm; D.M. 472/99). These values are not dangerous for human health but they can however have impact on the environment, for that reason Cu is classified as a primary pollutant.

The project RAMET provided a wide soil survey in the *Valle Versa*, a historic vine-growing area in the *Oltrepò region*, in order to study the environmental fate of copper (rate of soil accumulation, migration through the soil profile and to the surface and ground water)

Survey area and sampling sites

The survey

Description and sampling of five representative soil profiles (labeled as P001, P002, CP1, CP2 and CP3).

- Determination of Pseudo total concentrations of metals by *aqua regia* digestion (Atomic Absorption Spectrofotometry)
- Speciation of Cu conducted by selective and sequential extractions on some samples
- Data on solid transport (st) in the surface water and on ground water quality collected in earlier studies of the Dipartimento di Scienze della Terra, Università di Pavia (Vercesi, 2003; Sauer, 2004; Coldagelli, 2004) and of Provincia di Pavia (Sacchi et al, 2006)
- Water of the *Versa river* sampled and analyzed during some flood events in order to quantify the solid transport. Mineralogical and chemical analysis have been carried out on st.

Cu in soils

Heavy metals analysis show a Cu enrichment in the top layer, always in combination with Zn and Mn and occasionally with Cd and Pb. **This is shown in all soil profiles except for P002.**

- **In CP2** an highly enriched carbonatic horizon at 60 cm depth interferes with metal migration towards the deeper layers (particularly for Cu and Zn).
- **In CP3** a secondary enrichment of Zn and Pb in the top layer, as well as an undifferentiated concentration of Ni along the profile (a probable natural origin) is shown.
- **In P001** a strong enrichment of Cu, Zn and Pb occurs in the top layer; Cu migrated below the topsoil (even if the highest concentration is at 10 cm); anthropogenic contribution visible up to Bw horizon; other metals (Cd, Mn, Ni, Pb, Zn) retained within the A horizon
- **In P002** an enrichment of Cd and Mn in the layer 0-10 cm is shown. [P002 is the only profile without retention of Cu or Zn in the upper levels]. Cu absence and Cd and Mn presence are unexplained.

Heavy metals concentrations (above) and selective sequential extractions for Cu and Zn (below) in P001

- Correlations between **Cu and Zn** and between **Cu and Pb** ⟶ suggests anthropogenic origin.
- Correlations between **Cu e Mn** ⟶ leads natural Mn content [derived from alteration of ultrabasic and basic rocks]

Copper speciation made by selective and sequential extractions in CP1, CP3 and P001 soil profiles has shown that:

CP1 and CP3 are very similar:

- Over 60% of Cu is retained in the residual fraction and increases with depth; maximum values in the deep horizon; others fractions decrease with depth;
- Anthropogenic Cu distributed in all fractions and bound to soil minerals; in topsoil a prevalence of labile fraction (exchangeable and bound to O.M.) indicates a greater bioavailability .
- O.M. fraction retains most Cu in soil (about 20%) after the residual one; minority fractions bound to Fe-Mn oxides and Carbonates (lower than 10% in topsoil).

P001 (uncultivated vineyard) shows, compared with CP1 and CP3:

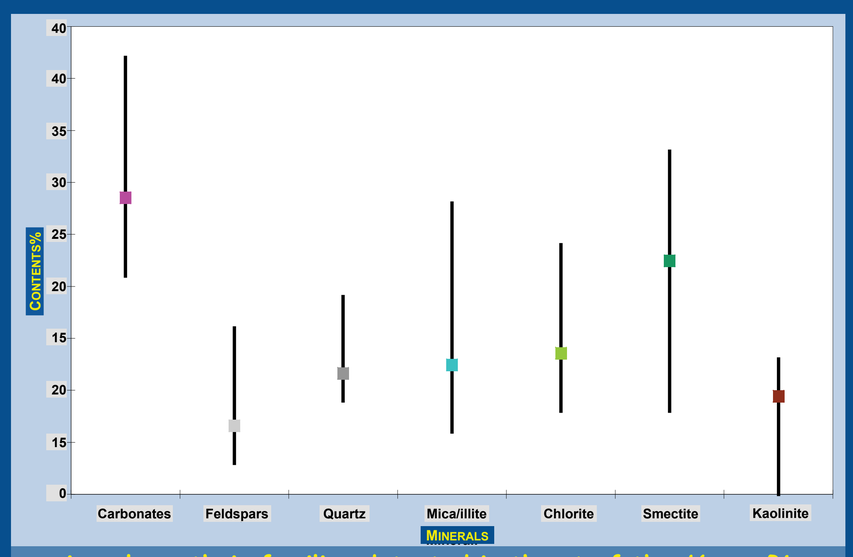
- Residual fraction less than that present in the O.M. (probable a greater competitiveness of O.M. in metals extraction); labile fraction bound to carbonates and oxides is very low (about 1% in topsoil) but increasing with depth.
- Speciation confirms Cu migration along the profile with labile phases moving towards deep horizons.
- Zn and Cu show a similar behaviour; however for Zn the exchangeable and bound to carbonates fractions are greater than the residual and bound to O.M. fractions.

Cu in surface water

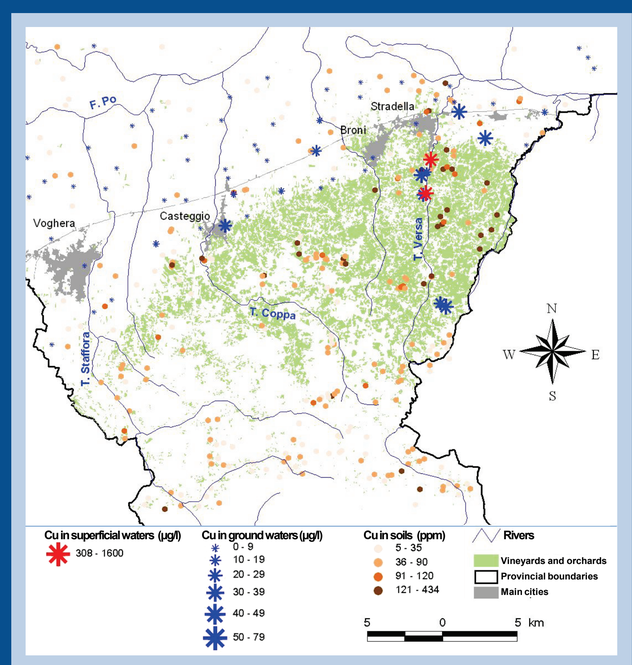
Samples of solid transport (st) collected from the Versa river in autumn and spring have shown that the grain size of st, depending on flood intensity, impacts on the mineralogical composition. Mineralogical phases are:

- Carbonates (about 30)
- Smectite (about 22%)
- other clay phases (about 30% in total)
- Feldspars (11%)
- Quartz (about 7%)

Mineralogical composition of st corresponds to that of medium and lower valley soils but highlights **a mineralogical variability which supports fine particles (clays and carbonates) depending on the erosive strenght of surface water, or rather on flood intensity.**



minerals or their families detected in the st of the *Versa River* (average, minimum and maximum%)



Cu concentration in *Valle Versa* soils and metals concentration in surface and ground water

Cu in ground water

- Cu concentrations in ground water (Vercesi, 2003) have values from 25 to 70 ppb (expected values in uncontaminated ground water: 3-5 ppb; Flemming and Trevors, 1989).
- Concentrations over 10 ppb in ground water are often observed along Apennine margin between Casteggio and Stradella (Provincia di Pavia, Sacchi et al., 2006).
- Presence of Cu in ground water confirms that the migration into streams could be a transfer mechanism of Cu to the water system (the primary recharge area of the Oltrepò pavese aquifer is in correspondence of the alluvial fan in the Apennine margin).

Conclusion

- In Lombardy the vine-growing area of Oltrepò is those where the long- lasting use of Cu-based pesticides causes the highest amount of Cu in soils, in association with Zn and occasionally with Cd and Mn;
- In the vineyards soils of the plain, Cu migrates vertically only, whereas in the hilly vineyards soils Cu mainly migrates laterally by run-off;
- Agricultural practices related to viticulture emphasize the soil natural predisposition to erosion and run-off, leading to a consistent solid transport of streams during flood events;
- Cu in soils is strongly fixed and poorly bioavailable, but its bioavailability increases in the process of erosion and transport because there is a selection for grain size and mineralogy towards Cu higher content and weakly bound fractions;
- A higher concentration of copper has been observed in ground water both in the hills and in the plain alongside vine growing areas.

The results of this study are published in a report (Regione Lombardia, 2007). The report is available for download on the website www.ersaf.lombardia.it

Acknowledgements

The project was co-funded by the Regional Direction for Agriculture (Regione Lombardia - d.g.r. 20733 of 16/02/2005) and by the Ministry of University and Research (PRIN 2004 - GEOBASI Geochemical Baselines of Italy).