FORMALDEHYDE: IS AN AIR CONTAMINANT IN RURAL AREA?

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Introduction

Formaldehyde (HCHO) is ubiquitous in the environment, it is an important endogenous chemical that occurs in most life forms, including humans, with an estimated Bioaccumulation Factor (BCF) of 3, calculated using a log Kow of 0.35 and a regression-derived equation.
HCHO production and its use in the manufacture of resins, disinfectants, preservatives, and a variety of other chemicals may result in its release to the environment through various waste streams.

It is formed naturally from:
- decomposition of plant residues in the soil, a well-known source of HCHO;
- decomposition of linalool in the atmosphere by ozone and/or OH and NO_3 radicals; the yields of linalool atmospheric decomposition into HCHO lies into the 30-40 % range;
- atmospheric decomposition of other biogenic VOCs such as isoprene and terpenes (like pinenes), the major VOCs naturally emitted by vegetation foliage (crops, trees, odoriferous plants, etc…). They react with hydroxyl radicals, forming HCHO as an intermediate product.

HCHO in rural areas could be also introduced in air through antropic activities as soil working, fertilization, soil sterilization and plastic film use (greenhouses, soil mulching, etc).

Formaldehyde

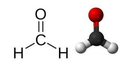
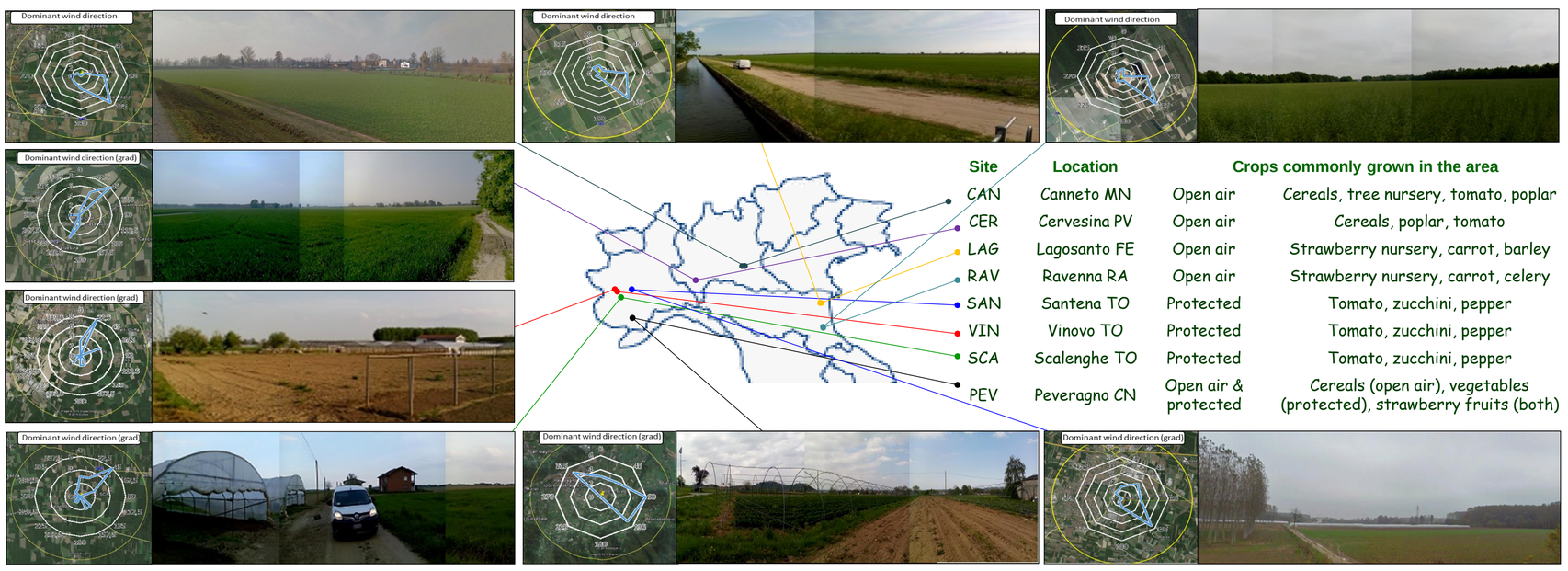
Structure	
Chemical name (IUPAC):	Methanol
CAS number:	50-00-00
EC Nr (from EINECS):	200-001-8
Formula:	HCHO
Molecular weight:	30.03
Mp/Bp	-92 / -19 °C
Vapour Pressure	> 1 atm at 20 °C
Solubility in water	400 g/100 mL
Density	0.8153 g/mL at 20 °C
US health exposure limits (NIOSH):	
- PEL (Permissible)	TWA 0.75 ppm (921,2 µg/m³)
- REL (Recommended)	TWA 0.016 ppm (19.7 µg/m³)
- IDLH (Immediate Danger)	20 ppm (24,56 mg/m³)

Table 1. HCHO chem/physical and tox characteristics

Objective

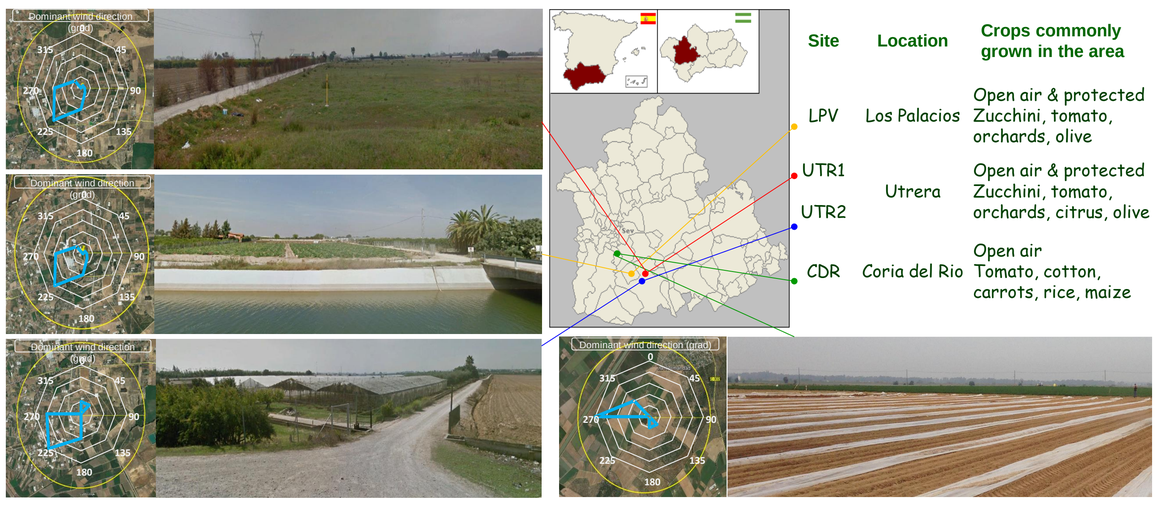
The main objective of this investigation was to enlighten the air level of HCHO in eight representative rural areas in Northern Italy and additional four sites in Southern Spain where human agricultural activities could play an additional role respect natural basal air concentration.

Material and methods:
8 rural sites monitored in Italy in May 2015, every 3 days for 5 times



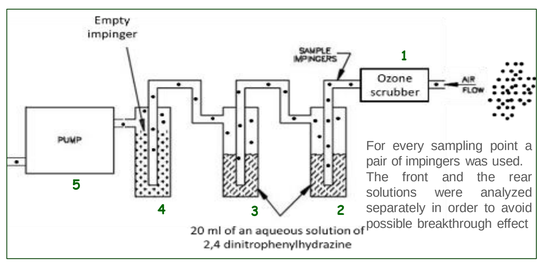
Site	Location	Crops commonly grown in the area	
CAN	Canneto MN	Open air	Cereals, tree nursery, tomato, poplar
CER	Cervesina PV	Open air	Cereals, poplar, tomato
LAG	Lagosanto FE	Open air	Strawberry nursery, carrot, barley
RAV	Ravenna RA	Open air	Strawberry nursery, carrot, celery
SAN	Santena TO	Protected	Tomato, zucchini, pepper
VIN	Vinovo TO	Protected	Tomato, zucchini, pepper
SCA	Scalenghe TO	Protected	Tomato, zucchini, pepper
PEV	Peveragno CN	Open air & protected	Cereals (open air), vegetables (protected), strawberry fruits (both)

Four additional rural sites monitored in Spain in April 2016



Site	Location	Crops commonly grown in the area
LPV	Los Palacios	Open air & protected Zucchini, tomato, orchards, olive
UTR1	Utrera	Open air & protected Zucchini, tomato, orchards, citrus, olive
UTR2		
CDR	Coria del Rio	Open air Tomato, cotton, carrots, rice, maize

Sampling procedure and analysis



- Air, drawn through an ozone scrubber KI cartridge (1) at 100 mL/min;
- Front (2) and rear (3) impingers (acid solution of derivatizing agent 2,4-dinitrophenylhydrazine [2,4-DNHP], 20 ml);
- Trap (4);
- Calibrated air sampling pump (5);
- Samples were collected over 8 hours, in 3 replicates per sampling event.

- Impinger solution quantitatively transferred into a flask and filled with water to a final exact volume of 25 mL
- Sample aliquot extracted twice with diethyl ether
- Extract taken to dryness and then reconstituted with acetonitrile
- Sample injected in LC-MS/MS system for qual/quantification of 2,4-dinitrophenyl-hydrazone

Presence of "background" level of HCHO (glassware and chemicals contributions)

Importance of control blank sample for every set of samples

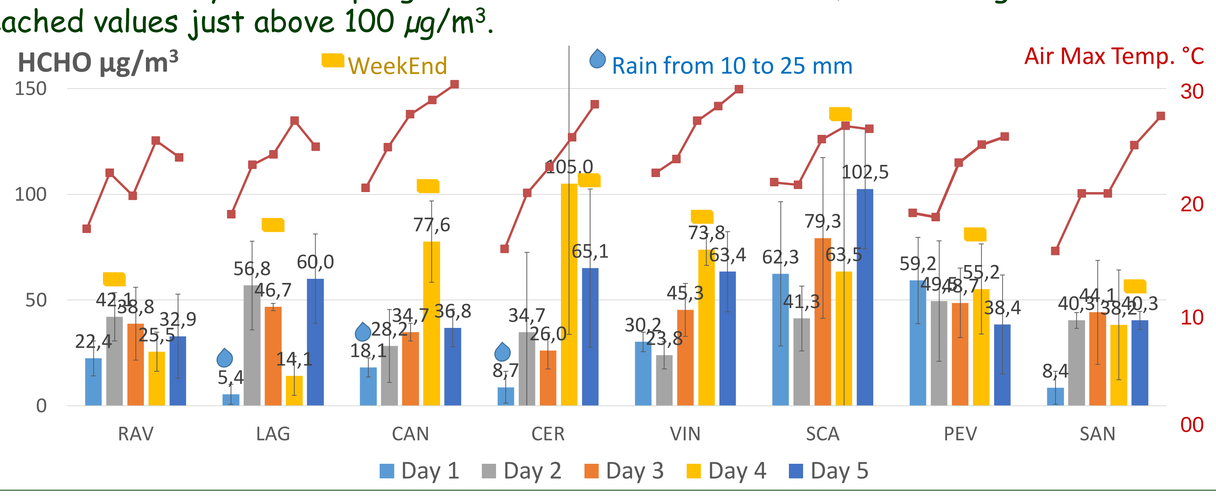
Samples results corrected by subtracting control blank

Results and Conclusion

HCHO was observed in all the sampling events, except one (site UTR1 - Spain, 2016), ranging from 5.4 to 105 mg/m³. When quantified, a significant standard deviation of HCHO concentrations was observed in each sampling time. This confirms the high fugacity of volatile chemicals and the need to avoid using single individual results for risk assessment purposes. Additional variability of concentrations was observed among sites, times and local climate conditions.
A statistical analysis of concentrations, obtained in a single site (site RAV - Italy, summer 2015, results not presented on this poster) over a period of 45 days, indicated a high level of correlation between atmospheric concentrations of HCHO and climatic conditions.

Italian sites

In the sites RAV and SAN, the average concentrations measured remained under 50 µg/m³ over the five days of sampling. In the sites CER and SCA, the average concentrations reached values just above 100 µg/m³.



Spanish sites

In the site UTR2, the average concentrations were less 81 µg/m³. Lower concentrations were found in the site CDR, rounding 25 µg/m³ while negligible concentrations were observed at LPV and UTR1.
In Spain the observed concentration of HCHO were lower than in Italian sites.