LIFE+11 ENV/IT/000002

CLEAN-ROADS

Action C2:
Monitoring the environment improvement of the project

D.C2.2

Report: Ex-ante impact evaluation

Project Coordinating Beneficiary	Provincia di Trento (PAT)
Project Associated Beneficiary n.1	Famas System (FAM)
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1. Introduction

Action C2 is one of the two project actions located within the action bundle C, which is responsible for the monitoring of the impact of the project actions. The objective of this action is to evaluate and monitor on a regular basis the environment improvements carried out within the project and in particular to analyze the positive impact that each action defined in the work plan has determined. The action is complementary to Action C1, which is responsible for the monitoring of the impact on the target audience and local welfare, and strongly connected to the activities carried out in Action E3 (Project Progress Monitoring), which is supervised by the Monitoring Committee, and is responsible to periodically assess the technical and financial progress of the project and to compare it with respect to the original plan. By including information about the measured impact of the project, the Monitoring Committee can be in the condition to assess how much effective the time and budget investments have been.

This document aims to present the results of the ex-ante impact evaluation concerning the task of monitoring the environmental improvement. In particular, this document:

- presents the targeted environmental problem (Chapter 2);
- describes the techniques used for the measurements of the monitoring indicators and the results obtained (Chapter 3).

2. Environmental problem characterization

The environmental impacts due to an excessive and non optimized use of de-icing chemicals on the roads during the winter season represent a relevant concern for the whole community; this project aims to specifically analyze and quantify them.

De-icing of roads during wintertime is achieved by spreading the road surface, whenever it is required, with a certain quantity of chemical compounds such as sodium chloride to lower the melting temperature of water. In Trentino, it is a common practice to use NaCl form salt mines as de-icing agent.

The salt, after being spread on road surface, can be removed by both wind and precipitation, as it is possibly to appreciate from the illustration of Figure 1. Due to wind action or dust resuspension caused by vehicles transit, salt is dispersed into atmosphere as particulate matters (PM). After meteorological events and precipitation, salt dissolves into water, becomes part of the superficial runoff and it’s flushed reaching superficial water bodies, aquifers, etc.

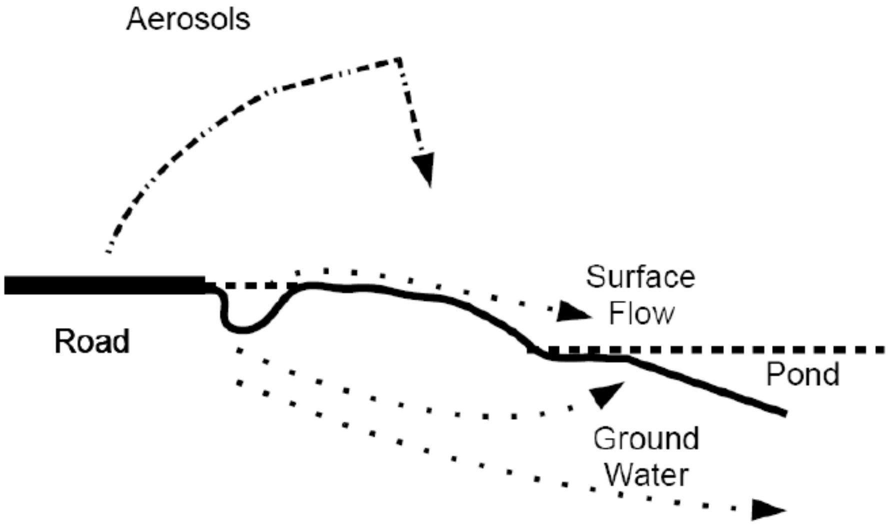


Figure 1: The salt dispersion process in the environment [1].

The aim of the entire environmental monitoring activity is to determine the local impact that chemical de-icing produce on air quality and aquatic systems and to quantitatively evaluate how the project is positively contributing in reducing this impact.

2.1. Impact on air quality

The Salting of the roads during winter leads to the accumulation of great amounts of dust on the streets. The dust can be flung in the air by the tires of the vehicles or raised by wind action, with the consequence of increasing the concentration of dust and fine particles in the air.

The atmospheric particulate matter consists of aerosol of various composition; it is commonly classified by its aerodynamic diameter, for instance the particulate PM_{10} is defined as particles behaving as spherical particles with diameter of 10 µm or less. High level of particulate in the atmosphere, and especially its finest fraction, has serious effects on human health and on environment. Epidemiological studies have shown strong correlations between high level of particulate and serious diseases due to its inhalation, including asthma, lung cancer, cardiovascular issues, respiratory diseases, etc. Furthermore, particulate contains mutagenic/carcinogenic compounds including polycyclic aromatic hydrocarbon (PAH) and toxic elements such as As, Cd, Ni, Pb, etc. In the recent years, the concern about the increasing levels of fine particulate in the atmosphere has been central in the public debate regarding air quality and health, both at European, national and local level.

2.2. *Impact on water quality*

De-icing salts based on NaCl and used in road maintenance are extremely soluble in water producing the ionic forms Cl- and Na+. Chloride is removed from roadways and transported during storm events causing a significant increase in the salinity of stormwater runoff. Half of the de-icing salts used on roads enters the aquatic environment via surface runoff, while the other half is transported into soils or groundwater. The negative impact of chloride on fresh waters and groundwater aquifers is a recognised environmental issue. It has been recently recognised a general increase in the salinity of freshwaters correlated with the use of road salts with the risk to approach the levels associated with negative effects of aquatic and terrestrial ecosystems. Other adverse effects of road salts are the alteration of the chemistry and density structure of lakes or the potential contamination of potable water supplies. Moreover, road salts application may result in chronic effects on biota such as detrimental effects on amphibians and in a decrease in aquatic biodiversity, associated for example to the enrichment of salt-tolerant and invasive species. Once contaminated by high chloride levels, surface and ground water can take decades, if not longer, to recover.

High concentrations of suspended solids and turbidity in the runoff water are another result of using de-icing salts coupled with sand. Solids and turbidity impact on aquatic plants, fish and invertebrates reducing photosynthesis while increasing mortality.

Therefore short-term preventive measures are required to reduce and optimise the seasonal use of salts and sand for de-icing the roadway with the aim to reduce pollutants production and the consequent environmental impacts.

3. Monitoring indicators measurement

3.1. Air quality indicators

For the evaluation of the impact of road salting practices on the air quality in Cadino we obviously had to measure reliably the concentration in the PM of any marker related with the chemical compound used as de-icing agent. Markers of NaCl are chlorine and sodium, but both these elements might be emitted by other sources. For instance, these elements are commonly found in the air masses moving over seas and containing sea salt spray but might be emitted by anthropogenic sources as well.

So unsurprisingly the European Commission Staff working paper SEC(2011) 207 "establishing guidelines for determination of contributions from the re-suspension of particulates following winter sanding or salting of roads under the Directive 2008/50/EC on ambient air quality and cleaner air for Europe" [2], states that the contribution to PM due to natural sources, including NaCl deriving from road salting activities, could be subtracted from the total concentration of particulate matter provided that it is clearly discriminated from that of any anthropogenic sources.

Previous experiences carried out in European regions aiming to quantify the impact of road salting activities on air quality rely on the fact that re-suspension of NaCl by traffic preferentially causes the emission of PM2.5 (aerosol with aerodynamic diameter of 2.5 μm) so that by measuring the PM10/PM2.5 ratio (ratio between concentration of aerosol with aerodynamic diameter of 10 μm and 2.5 μm, respectively) it was possible to recognize pollution episodes due indeed to the spreading of salt. Nevertheless, this same approach applied in Austria apparently indicated that road salting activities do not affect air quality. Austria certainly has strong similarities with Trentino from the point of view of climate and potential occurrence of anthropogenic sources of chlorine and sodium. Therefore, it was supposed that any attempt to evaluate the effect on air quality due to road salting practices could have been unsuccessful if based on the same approach. On the other hand, during previous investigations carried out in Trento we observed a remarkable increase of the concentration of these elements in PM10 during wintertime.

Trends of Cl^- and Na^+ (chlorine and sodium from NaCl are water-soluble and are easily measured in their ionic form) in PM10 samples collected in Trento from Nov. 12, 2012 till Jun. 30, 2013 are shown in Figure 2. It is evident from Figure 2 that the concentration of Cl^- and Na^+ increases to values far exceeding 0.5 $\mu g/m^3$ from the beginning of Dec. 2012. Concentrations then gradually decrease to the background levels from mid of Jan. 2013. It can also be observed that the Cl^-/Na^+ ratio is not constant but rather spans over values from about 0.5 up to more than 3. The value hardly never equals 1.5, corresponding to the stoichiometric ratio of chlorine/sodium in NaCl.

These observations suggest that emission of chlorine and sodium is likely related to road salting activities, long range transport of sea salt and to anthropogenic sources. Besides, the high concentration of Cl^- and Na^+ during wintertime indicates that the contribution of these sources remarkably affect the air quality.

These results also suggest that the identification of the sources of chlorine and sodium possibly affecting air quality in Cadino would be hardly achieved provided that limited information of PM composition (namely concentration of chlorine and sodium only) were available. Unfortunately, no other chemical markers of the salt used for road maintenance exist, to our knowledge. Therefore, a detailed investigation of the chemical composition of PM10 was performed in the framework of the Clean-roads project and multivariate analyses/source apportionment tools such as Positive Matrix Factorization (PMF) were applied to identify the sources of PM10.

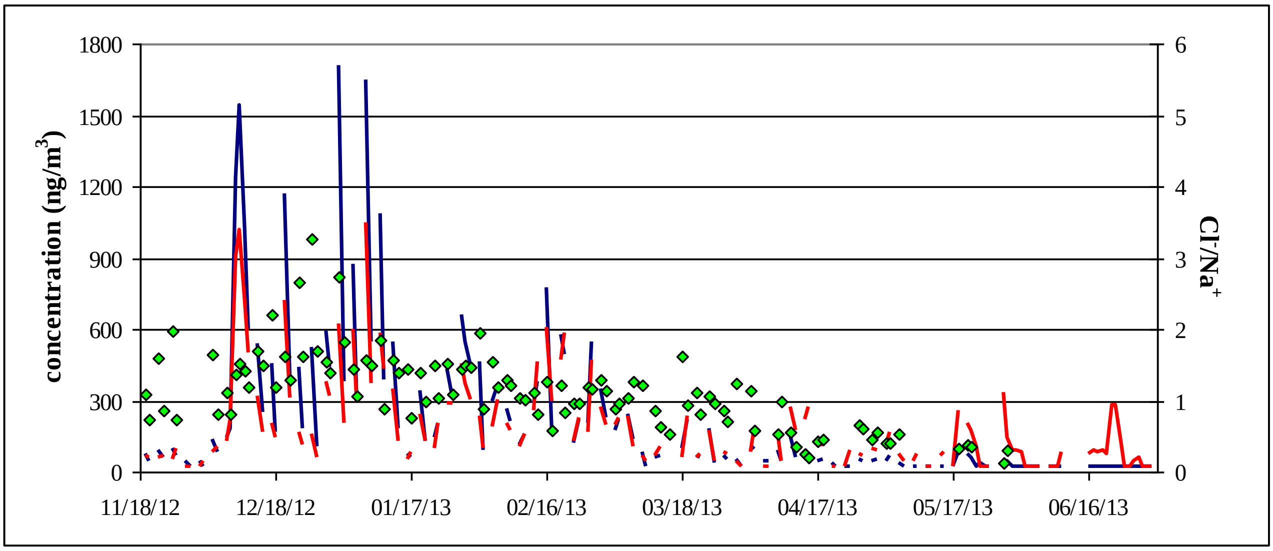


Figure 2: Concentration of Cl$^-$ (blue line) and Na$^+$ (red line) in PM10 samples collected in Trento (on left axis). Cl$^-$/Na$^+$ ratio (green line) on the right axis.

3.1.1. Data collection

The atmospheric particulate matter consists in a various composition of aerosol and particles, and it is commonly classified by its particles diameter. PM10 is defined as the particles with diameter of 10 µm or less.

According to Directive 2008/50/EC on ambient air quality and cleaner air for Europe, the reference method for the sampling and measurement of PM10 is that described in EN 12341:1999 [3].

PM10 concentration is obtained by gravimetric analyses. Ambient air is passed through a size-selective inlet at a known, constant flow rate. The relevant PM fraction is collected on a filter for a known period of nominally 24 h. The mass of the PM material is determined by weighing the filter at pre-specified, constant conditions before and after collection of the particulate matter.

A climate-controlled facility is used for conditioning and weighing the filters. The balance used is installed and operated within the weighing room and has a resolution of 0.10 µg.

Prior to sampling, all filters are uniquely identified, conditioned in the weighing room at (20±1)°C and (50±5)% relative humidity for more than 48 h, and then weighed.

In order to collect PM10 on filters, we used a Tecora Skypost PM HV, an automatic outdoor station for continuous atmospheric particulate monitoring. The system stores up to 16 filtering membranes. The automatic sequential substitution of the filtering membrane and the electronic flow rate controller allow continuous, unattended operations as well as an easy replacement of the exposed filters without interrupting the sampling. Skypost PM HV was used for dust sampling with LVS PM10 2.3 m^3/h sampling head, according to EN 12341 norm [3, 4].

After sampling, all filters are conditioned in the weighing room for more than 48 h and then weighed.

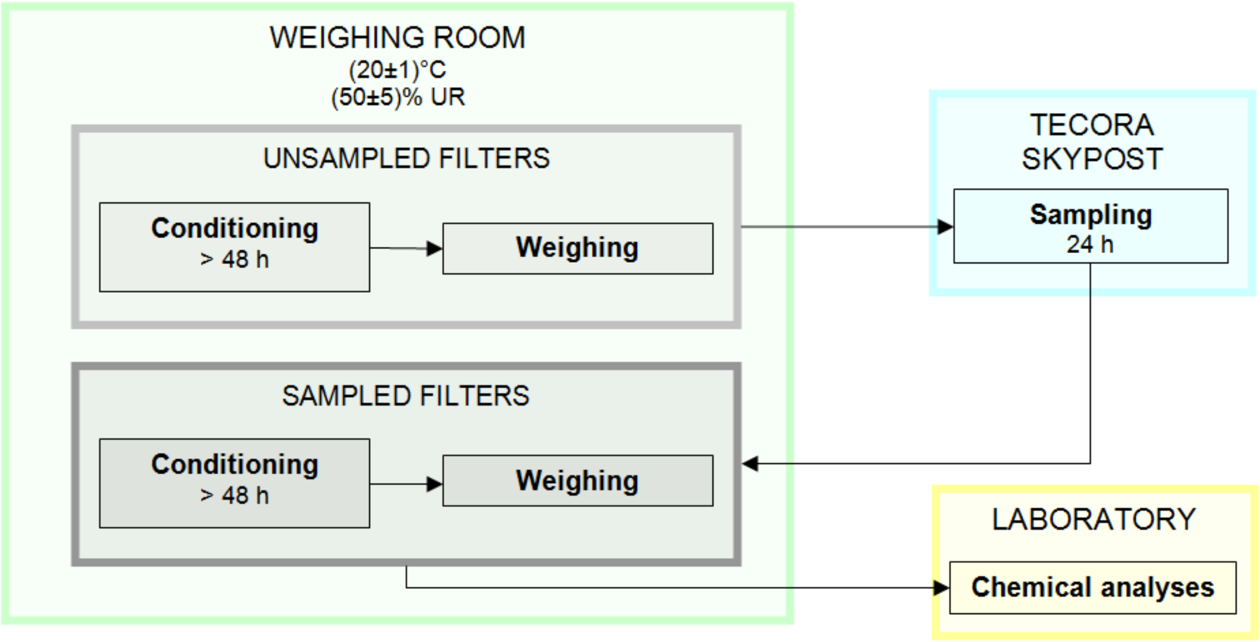


Figure 3: Flow chart.

Measurement result, expressed as µg/m³, is calculated as the difference in mass between the sampled and unsampled filter, divided by the sample volume, determined as the flow rate multiplied by the sampling time:

$$c = \frac{m_l - m_u}{\varphi_a \cdot t}$$

where:

c is the concentration, in µg/m³;
m_l is the sampled filter mass, in µg;
m_u is the unsampled filter mass, in µg;
φ_a is the flow rate at ambient conditions, in m^3/h;
t is the sampling time, in h.

The standard set of chemical analyses of PM10 samples included metals (EPA method IO-3.3 [5]), water soluble ions (ion chromatography), polycyclic aromatic hydrocarbons (PAH, according to ISO 16362:2005), levoglucosan (GC-FID), and carbon (both organic and elemental by thermal method).

Metals embrace markers of PM10 from crustal origin (Al, Si, Ti, Ca, Fe and road erosion), traffic (Fe and minor elements used in engines, brakes and tires) and industrial sources. Soluble ions include of course Cl^- and Na^+ but also markers of secondary PM10 and other sources. PAHs are toxic organic compounds produced by combustion processes of fossil fuels and biomasses and are thus markers of traffic and, for instance, wood combustion for domestic heating. Levoglucosan selectively forms during the combustion (pyrolysis) of cellulose and it is a specific marker of biomass burning. Finally, organic and elemental carbon is related to combustion processes (traffic, domestic heating) and, the former, also to secondary generated aerosols.

PM10 samples were collected daily in Cadino non only during wintertime, but also in summer (discontinued) in order to recognize possible anthropogenic sources of chlorine and sodium. Sampling of PM10 started on July 5, 2013 and ended on April 17, 2014.

The chemical dataset consists of 219 samples and a total of 8656 data, including gravimetric analysis of PM10. Samples were collected using Teflon membranes or quartz filters. Source apportionment was carried out using EPA PMF ver. 5.0 [6].

3.1.2. Results and discussion

Winter 2013-2014 (December 2013 - February 2014) was particularly anomalous both in our region and in the rest of Italy and also in Europe. On the regions of central and northern Italy, in particular, this season was one of the most hot and rainy observed in the last 100 years, characterized by temperatures well above the average and by frequent and abundant rainfall, especially on alpine areas. This significant meteoclimatic anomaly has strongly impacted also on air quality. In all Trentino monitoring sites, we observed low pollutants concentrations, not representative of a "normal" winter. PM10 concentration was 25% lower than the average values of last 5 winters. In addition, during last winter, we observed only in few days concentrations exceeding the daily limit (50 $\mu g/m^3$). Also in Cadino, PM10 concentration was low, and the daily limit was exceeded only 2 times (Figure 4). Therefore, winter 2013-2014 wasn't representative of a normal winter.

Trends of Cl^- and Na^+ in PM10 samples collected in Cadino are displayed in Figure 5. This figure shows that concentration of Cl^- and Na^+ hardly exceeds 600 ng/m^3 and that again the Cl/Na ratio spans over a range extended from about 0.5 up to more than 5. These results indicate that concentrations of chlorine and sodium during winter 2013/2014 were slightly reduced compared with the amounts measured in Trento during winter 2012/2013 (see Figure 2). Interestingly, a lower concentration of Cl^- and Na^+ is also observed in PM10 samples collected in Trento in winter 2013/2014. A reduced concentration of Cl^- and Na^+ observed for different sites during the same period suggests that anthropogenic sources of chlorine and sodium / re-suspension following road salting very likely predominates over long range transport of sea salt, although the occurrence of these latter phenomena might undergo remarkable variations from time to time.

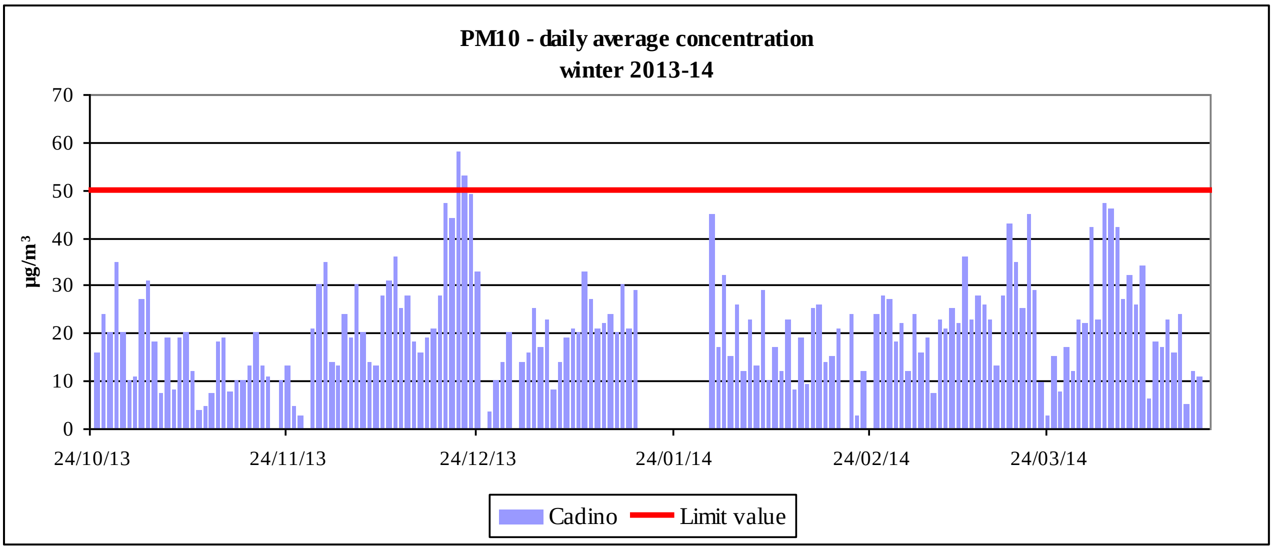


Figure 4: PM10 daily concentration.

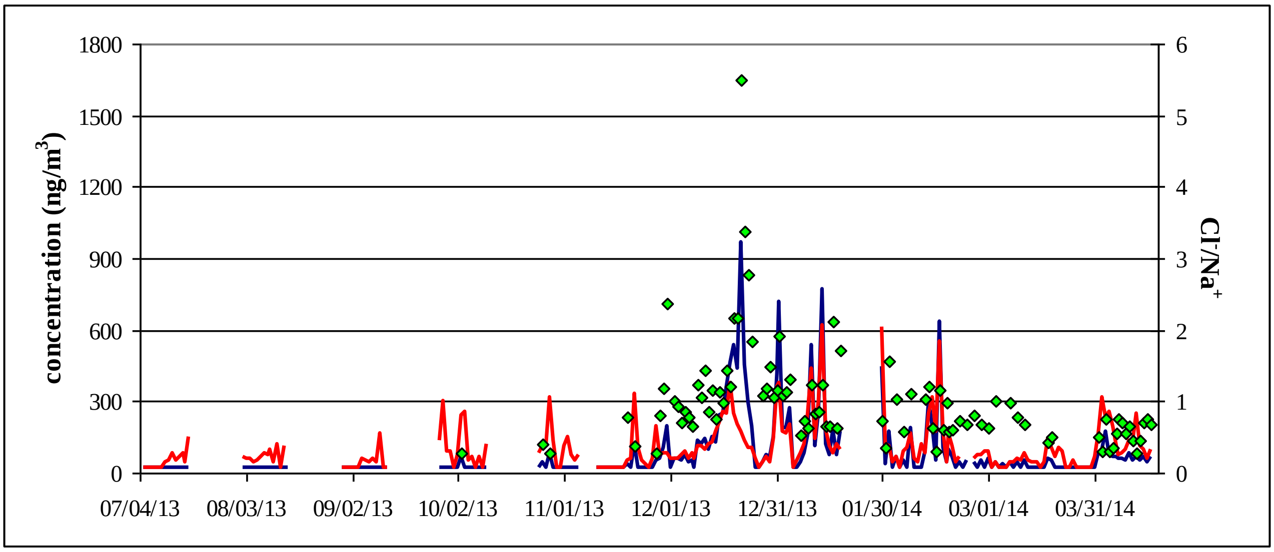


Figure 5: Concentration of Cl- (blue line) and Na+ (red line) in PM10 samples collected in Cadino (on left axis). Cl-/Na+ ratio (green line) on the right axis.

Positive Matrix Factorization of experimental data reveals 6 main sources to be accountable for the concentration of particulate matter in Cadino. For a sake of clarity, only the sources related with the presence of chlorine and sodium will be discussed in the following.

Chlorine is present in the emission profiles of two sources. About 30% of chlorine is distributed in a profile characterized above all by a high concentration of levoglucosan, PAHs, elemental and organic carbon and soluble potassium. This emission profile is recognized as due to “biomass burning”. About 70% of chlorine appears to be related with a second source having a simple emission profile largely dominated by chlorine and sodium. Because of the absence of other markers, this source is identified as due to the re-suspension of pure NaCl, namely “road salting”.

Also sodium is mainly due to “road salting” (71%) but it is also present in the emission profiles of two other sources. About 12% of sodium is present, along with several transition metals, carbon, and a small amount of PAHs, in the profile of a source identified as due to “traffic”. About 15% of sodium is finally present in a profile largely dominated by $SO_4^=$, its counter-ion NH_4^+ and lower amounts of trace elements. This source is identified as “secondary sulphate”. The remaining sources of PM are identified as “re-suspended crustal materials” and “secondary nitrate”.

Despite that the PMF emission profile of “road salting” is very similar to what it is expected from the re-suspension of pure NaCl from salt mines, it has to be observed that the measured Cl/Na ratio is about 1. This value is lower than the theoretical stoichiometric value of NaCl (1.5). Scatter plot of experimental vs. PMF predicted concentration for chlorine (reported in Figure 6) on the other hand, points out that PMF underestimates, on average, the concentration of chlorine being actually present in the samples. As reported by Figure 6, the slope of the linear fit is 0.70 and correlation coefficient (R^2) is 0.75, suggesting that chlorine is not completely described by the 2 sources. Conversely, the slope for sodium is 0.88 and R^2 is 0.97. Both values are reasonably close to unity. These results indicate that sodium concentration in PM10 is indeed very well modelled by 3 sources.

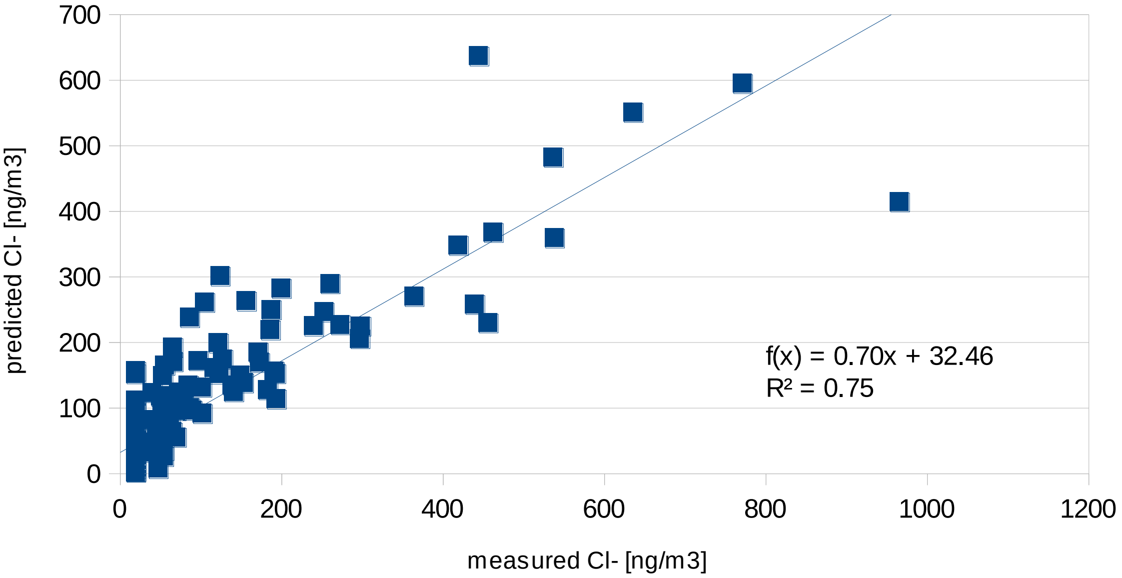


Figure 6: Measured vs. PMF predicted concentration of Cl^- in PM10 samples collected in Cadino.

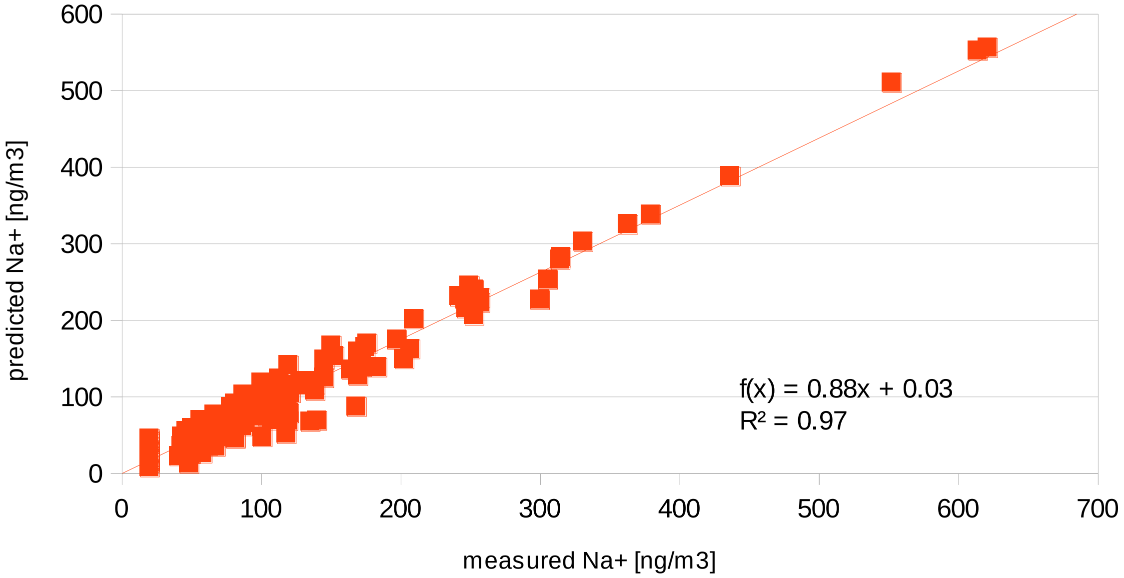


Figure 7: Measured vs. PMF predicted concentration of Na^+ *in PM10 samples collected in Cadino.*

Parallel investigations of PM composition in rural sites where air quality is heavily affected by combustion of wood for domestic heating confirm the co-emission of chlorine and levoglucosan upon “biomass burning”. “Biomass burning” is thus assumed to be the main anthropogenic source of chlorine also biasing PM composition in Cadino. PMF does not highlight any additional source of chlorine. However, sporadic arrival of air masses transporting PM with relatively high concentration of chlorine has been observed. In this regard it is worth mentioning that such events are hardly predicted by any multivariate analysis tool.

Episodes recognized by PMF as due to “road salting” are reported in Figure 8, along with the records of salt spreading. Concentration of particulate matter apportioned to “road salting” (in blue) is reported on the left. Actual salt spreadings (in red) are classified according to the density of NaCl distributed per unit area.

It can be seen from Figure 8 that the observed trends of PM concentration apportioned to “road salting” and actual NaCl spreading are not always in agreement. In particular, random events classified as “road salting” are detected from November 2013 until mid of December 2013, when no actions took place indeed. No activities were performed on Dec. 18, 2013, when the concentration of PM due to “road salting” reached a local maximum. The first activity was executed on Dec. 19, 2013, and several others took place in the following days but a clear increase of PM concentration due to “road salting” was observed on Dec. 31, 2013. The maximum concentration of PM recognized as “road salting” was on Jan, 13, 2014 but actually the largest amount of NaCl was spread on Jan. 14, 2014. A perfect agreement was then observed for the activities performed on Jan. 30, 2014, Feb. 11 and Feb. 14, 2014. For all these cases, the increase of PM concentration apportioned to “road salting” was immediate or closely subsequent.

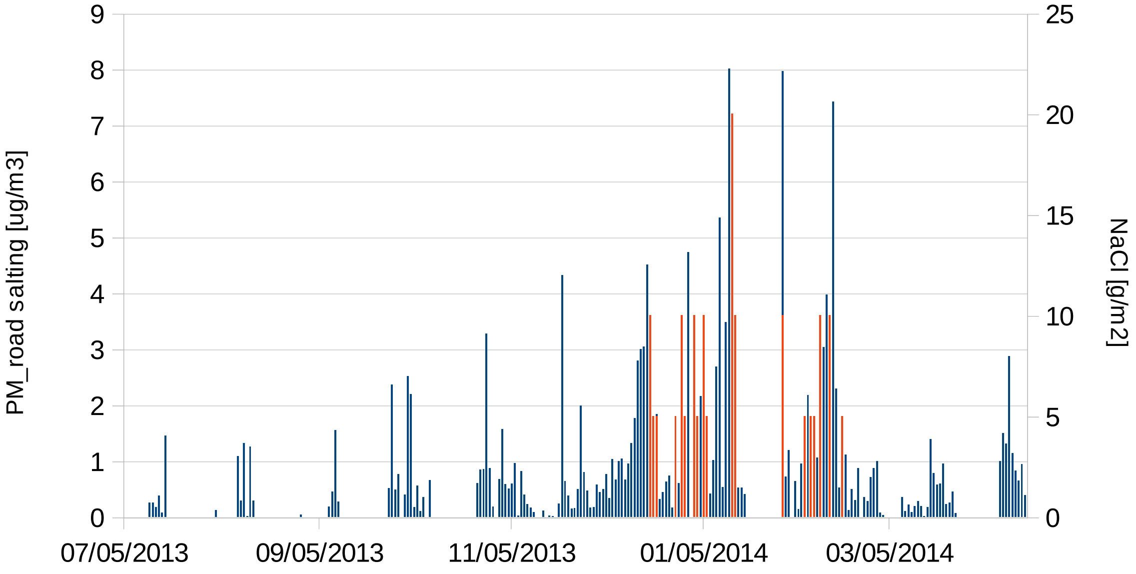


Figure 8: “Road salting” according to PMF (in blue) and actual NaCl spreading (in red).

3.1.3. Conclusions

Preliminary investigations of the effect of road salting activities on PM concentration performed by investigating a number of chemical markers indicate clearly the occurrence of an anthropogenic source of chlorine (“biomass burning”) and additional sources of sodium (“traffic” and “secondary sulphate”). A correct estimation of the contribution of road salting on air quality can not be performed by simply measuring the concentration of chlorine and sodium but rather requires an approach where several markers of PM sources and source apportionment/multivariate methods are used.

In spite of these noticeable findings, the identification of the pollution episodes related to NaCl spreading is not always undeniable. PMF partially underestimates chlorine content in PM samples and classifies as “road salting” pollution episodes that are actually not due to this practice. Multivariate methods such PMF on the other hand confirmed to be powerful tools. Different model run approaches will therefore be tested, including constrained model operation, to evaluate the accuracy of PMF for “road salting” source identification and apportionment.

A different sampling strategy will also be introduced and the analytical procedures for detecting chlorine and sodium will be slightly modified. Quartz filters require pre-firing prior to use, a process that could introduce cross-contaminations. So teflon membranes only will be employed for PM sampling in order to reduce the frequency and magnitude of the random analytical errors. Finally, a larger sample aliquot will be used to lower the detection limits. These modifications will certainly improve the accuracy of the experimental data.

3.2. Water quality indicators

The pollutant loads in runoff water (chloride, solids, turbidity, …) produced from the use of de-icing salts and referred to in the literature show a high variability which suggests the need for site-specific monitoring and intensive campaigns in order to avoid biased estimations [7,8]. An accurate site-specific monitoring of water quality represents thus a key requirement to adequately explain the complex response to a rainfall or a snow event.

The runoff volume (V) produced from the watershed or the flow rate (Q) during one storm event can be theoretically calculated taking into account the rainfall depth (P) or the intensity (i), the contributing catchment area (A) and the runoff coefficient (φ) according to the calculation $V = \varphi \cdot P \cdot A$ or $Q = \varphi \cdot i \cdot A$, where φ assumes values of 0.7-0.95 for asphalt pavement. Although this expression is widely used for estimating stormwater runoff, it is not accurate to be used for the calculation of pollutant loads, especially during winter periods when rainfall may happen with melting of snow. Therefore the runoff flow rate was measured in the monitoring site to obtain continuous site-specific data.

For instance, the rainfall intensity over time (hyetograph) and the corresponding runoff flow rate (hydrograph) is shown in Figure 9A. In general, a time delay exists between the initiation of the rainfall and the initiation of the corresponding runoff, which depends on the size of the contributing area. In our case, considering the monitoring station very near the road, a short delay is expected due to the short transport time.

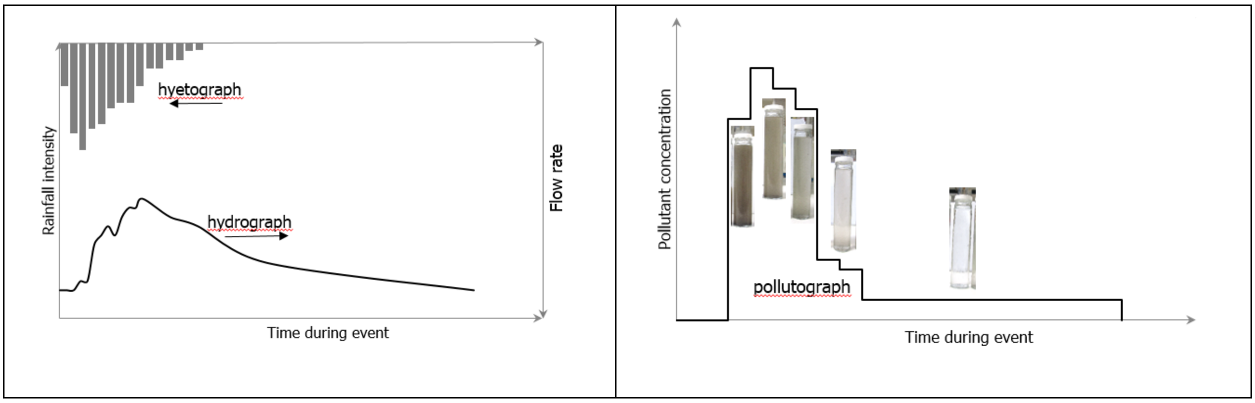


Figure 9: (A) Rainfall intensity over time (hyetograph) and the corresponding runoff flow rate (hydrograph). (B) Pollutograph during a runoff event.

The plot of the concentration of pollutants as a function of time is defined as a pollutograph (Figure 9B) and it is obtained from a discrete sampling during the runoff event. In general, the peak of concentration in the runoff appears in the first minutes, caused by the early runoff which transports the accumulated pollutants from the road surfaces. After the peak, the pollutant concentration decreases progressively and may remain approximately stable in the final part of the profile. In many cases, the pollutant concentration peak may precede the flow peak: this phenomenon is called first-flush. When the first-flush occurs for a pollutant, it means that a large fraction of this pollutant is contained in the initial runoff. This has an immediate implication: the first-flush part of the flow should undergo treatment to reduce pollutant loads before utilization or discharge into receiving waters. The occurrence of a first-flush depends on rainfall intensity and duration and on characteristics of the catchment. In particular, an inverse relationship is referred between the strength of first-flush and the watershed area [9]. Therefore an evident first flush is expected in the monitoring of road runoff due to the small area contributing to the runoff.

A synthetic parameter to describe the runoff quality is the "event mean concentration" (EMC, expressed in mg/L) which can be calculated from the pollutograph with a flow-weighted estimation or measured as flow-proportional average concentration during a storm event. EMC is defined as the total mass of a pollutant transported during an entire runoff event (M) divided by the total stormwater runoff volume (V) according to the following expression:

$$EMC = \frac{\sum_{i=1}^{N} C_i \cdot V_i}{\sum_{i=1}^{N} V_i}$$

where, N is the total number of samples collected in the runoff event; i (1,2,…,N) is the sampling sequence number in the event; Ci is the pollutant concentration in sample i; Vi is the discharged runoff volume corresponding to sample i.

A large variability of runoff quality and quantity is always observed during each event and during a season. It is well known that a few grab samples during one storm event are not representative of a whole winter season. The design of a representative monitoring campaign has to be based on intra-storm sampling and inter-storm sampling. The intra-storm sampling design includes the analysis of more samples along the event which permit to obtain the pollutograph. Because of the unpredictability of rainfall during the storm event, sampling will always involve some uncertainty. Therefore, optimisation of the monitoring was performed with an user-defined sampling. In this case the sampling time was varied with the aim to optimize the sampling, on the basis of real-time control of on-line instruments by using remote programming.

With regards to the number of runoff events sampled during the winter period, the decision is problematic because it depends on many factors. In fact, precipitations always have a very high intrinsic variability and it is difficult to do previsions. A complete runoff monitoring program should include events with different characteristics, including various rainfall intensities, durations, included snowfall. To avoid subjectivity in the selection of the events for sampling, all the runoff events occurred during the period of using road salts were considered. In particular, events with signals of water level, turbidity or conductibility (the installed equipment) above the detection levels were monitored. In this project, the inter-storm sampling design carried out during the winter 2013/2014 included the monitoring of 11 events.

3.2.1. Data acquisition

Data acquisition about quality and quantity of runoff water is an open issue [10] and there is not a unique procedure suitable for all monitoring studies. Thus, in this work, a specific procedure was developed for monitoring the runoff produced by rainfall and snowmelt, according to the best practices in the literature. The monitoring campaign during the winter 2013/2014 involved rainfall measurements, flow-rate estimation, collection of a significant number of samples and analyses of various contaminants. Operators visited the monitoring station every 2 weeks for routine maintenance of the instrumentation, while the samples automatically collected by the samplers were taken immediately after sampling to carry them to a laboratory for analyses.

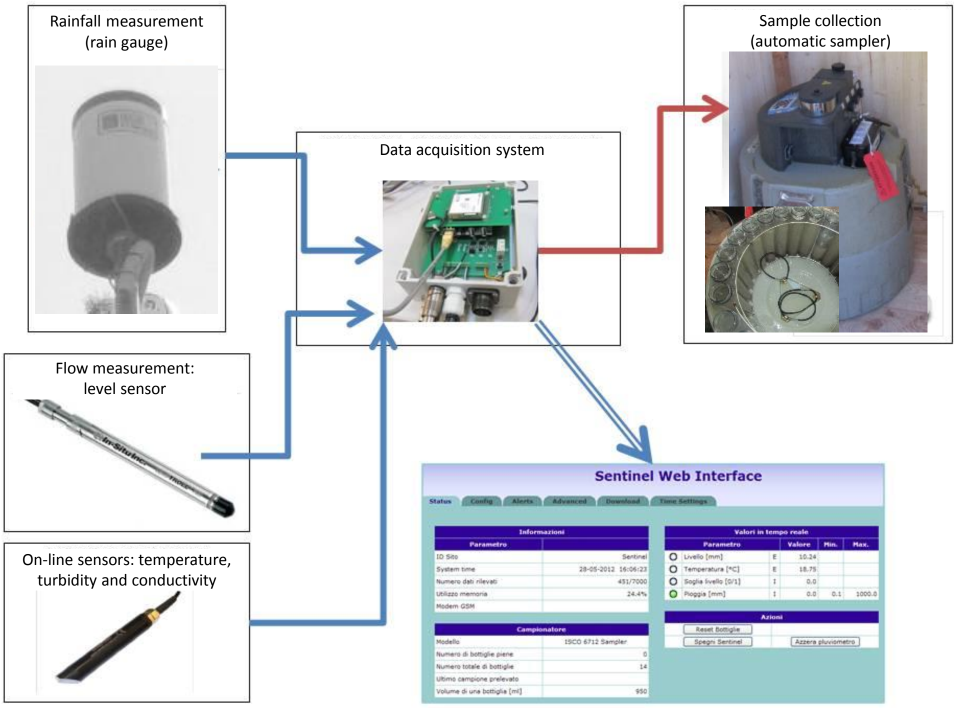
A number of 11 rainfall/snowfall events were monitored continuously with on-line instrumentation from December 2013 to March 2014.

The monitoring station

The selection of the site for monitoring the runoff water was aimed at facilitating representative sampling and flow measurement of water, including the following features: a separate water drain system, an open channel for measuring flow rate, a place that is safe to be reached by field personnel, and suitability for installing sampling equipment.

The equipment installed for water monitoring was composed by various devices connected together which included (Figure 10):

- a rain gauge for in-situ measurements of natural rainfall
- a water level probe for measuring runoff flow rate
- an automatic sampler for sample collection
- various on-line sensors for in-situ monitoring of water quality
- electronic instrumentation to record and transmit data via cellular phone connection.



Informazioni	
Parametro	
ID Sito	Sentinel
System time	28-05-2012 16:06:23
Numero dati rilevati	451/7000
Utilizzo memoria	24.4%
Modem GSM	

Campionatore	
Modello	ISCO 6712 Sampler
Numero di bottiglie piene	0
Numero totale di bottiglie	14
Ultimo campione prelevato	
Volume di una bottiglia [ml]	950

Valori in tempo reale					
Parametro			Valore	Min.	Max.
○	Livello [mm]	E	10.24		
○	Temperatura [°C]	E	18.75		
○	Soglia livello [0/1]	I	0.0		
●	Pioggia [mm]	I	0.0	0.1	1000.0

Azioni

Figure 10: The equipment installed for water monitoring.

The following sections describe more in depth some characteristics of the installed devices.

Rainfall measurement

Although the on-line monitoring of rainfall events is a key parameter to determine when to start sampling by automatic samplers during common stormwater events, in the case of runoff produced by snowmelt, the runoff might be not necessarily associated with rainfall. However, local rainfall data acquired as close as possible the monitoring station are important to give a more complete description of meteorological conditions in a monitoring period. In this study, the rainfall depth was measured with a tipping bucket rain gauge (model ISCO 674) with a resolution of 0.1 mm, which consists of a funnel that collects the rainwater and channels it into one of two compartments of a bucket. When the bucket tips (for instance, after 0.1 mm of rainfall), an electrical signal is recorded, to give the cumulative rainfall (expressed in mm) or the rainfall intensity (expressed in mm/min or mm/h).

The data of rainfall depth measured by the rain gauge (on-site data) were compared with data acquired by one meteorological stations located in the area (off-site data) but a few kilometres far from our monitoring station. In all the rainfall events, a difference was found between on-site and off-site data, as expected, considering the different location of the devices, but this difference did not affect significantly our study.

The rain gauge allows only liquid precipitation to be quantified. Snow events were identified by an on-line optical sensor based on a red laser and placed at the monitoring station. This sensor permitted to distinguish between snowfall, rainfall, hail and mixed precipitations and to classify them according to their level of intensity (zero, low, medium, high). It did not permit calibration against measurements from a rain gauge and thus it was used only for a qualitative detection of snow events (whether it was snowing or not). When useful, the quantification of snowfall was obtained from another one meteorological stations located in the area (off-site data).

Flow measurement

Accurate flow measurement is essential in the monitoring of runoff water and for the determination of the pollution loads. In this project, continuous measurements of flow rate (in time steps of around 1 min) were performed in an open channel where the hydraulics is controlled using a triangular weir. The discharge through the triangular weir is directly related to the depth of the flow measured by a water level probe (Level Troll 500, In-Situ nc.). Flow rate is then calculated using curves based on the geometry of the standard triangular weir.

Velocity-based devices based on area–velocity sensors, although widely applied in flow analysis, were excluded in our monitoring of snowmelt runoff, because with small flows, measurements may be intermittent and the probe may be susceptible to accumulation of sediment or litter.

Sample collection equipment

An automated sampler (model ISCO 6700) was installed in the monitoring station for collecting a series of samples which can be analyzed individually or composited. The automatic sampler was set to trigger the sampling of water with aliquots 0.5 L on receipt of one of the following signals: (i) water level at a certain depth or (ii) a certain value of an on-line sensor such as conductivity or turbidity. For example, when the water level in the open channel reached a pre-determined set-point after the beginning of a rainfall or snowfall event, the automatic sampler began to sample.

A time-proportional sampling of discrete samples was performed in the monitoring campaign. This means that discrete samples of equal volume were collected at equal increments of time. As for the sampling intervals, samples were collected at 15-min intervals, while intervals were extended to 30 min or some hours during periods of slow melting of snow. The samples were collected as discrete samples.

A number of 5 rainfall/snowfall events were fully monitored with the collection of various samples: (i) 24-26 December 2013, 5 samples, (ii) 04-06 January 2014, 6 samples, (iii) 14-18 January 2014, 4 samples, (iv) 07-09 February 2014, 6 samples, (v) 13 February 2014, 4 samples.

Unsampled volumes occurred as the result of signals below set-points for triggering sampling or stormwater flow lower than the sampler pump intake. No accidental equipment malfunctions or breakages occurred during the winter 2013/2014.

In-situ on-line sensors

Temperature, turbidity (a surrogate parameter of suspended solids) and conductivity were measured in-situ using on-line sensors installed in a funnel above the open channel which permit instantaneous and continuous monitoring.

Turbidity was measured with a digital turbidity sensor (PONSEL Mesure – Group Aqualabo). Conductivity was measured with two instruments to avoid occasional loss of data: (i) SC 200 instrument equipped with a 3798-S sc sensor, provided by Hach-Lange and (ii) DL/N70 instrument provided by STS Italia.

Data were collected every minute and they were available remotely by a GSM connection. In the monitoring campaign of winter 2013/2014 the routine maintenance of the probes (every 2 weeks) was enough to guarantee proper operation without the need of a further frequent maintenance.

Other installations

All the instrumentation included in the monitoring station (sampler, data logger, etc.) was placed in a dedicated structure suitable for routine servicing and operation and to avoid any damage from the weather or vandalism. The data acquisition system of the monitoring station was connected to all the sensors and was based on an interface for: (i) on-site manipulation (ii) remote programming via a telephone modem. Data stored were downloaded to a portable PC or to a host PC via a modem.

Analytical parameters

After collection, samples were transported and analyzed in the laboratory of the partner. The physico-chemical parameters analysed in the runoff water are indicated in Table 1.

Parameter	Method of analysis
Total suspended solids (TSS), cyanide	Standard Methods (APHA, 2012) [11]
pH, electrical conductivity	Rapporti ISTISAN 2007/31 [12]
Fluoride, chloride, nitrate, sulphate	APAT CNR IRSA 4020 Man 29 2003 [13]
Ammonium, sodium, potassium, litium, calcium, magnesium	APAT CNR IRSA 3030 Man 29 2003 [13]
Alluminium, arsenic, barium, boron, cadmium, chromium, iron, phosphorus, manganese, nickel, lead, copper, zinc.	APAT CNR IRSA 3020 Man 29 2003 [13]

Table 1:Parameters analysed in the runoff water and methods used for the analyses.

TSS is a common bulk parameter to determine the content of solids in stormwater, after filtration of samples on 0.45 µm membrane filters (for the separation of suspended and dissolved fractions). TSS measured in the laboratory is often correlated with the on-line measurement of turbidity. Electrical conductivity was measured in the lab and compared with data measured on the field with in-situ sensors.

Heavy metals were also analysed in a few monitoring campaigns of runoff water during the winter period. The relevance of heavy metals, such as such as alluminium, cadmium, chromium, nickel, lead, copper, zinc derived from traffic and roads is related to their potentially toxic effects on biota. Iron is not generally considered a pollutant in runoff water. Because heavy metals are most toxic in their dissolved form, the analyses were also performed with and without filtration of the samples on 0.45-µm membrane, to separate metals in the dissolved and particulated forms.

Lab analyses were performed on 5 rainfall/snowfall events: (i) 24-26 December 2013, (ii) 04-06 January 2014, (iii) 14-18 January 2014, (iv) 07-09 February 2014, (v) 13 February 2014. In total, 25 samples were analysed corresponding to a total number of 738 analyses.

3.2.2. Results and discussion

All the runoff events occurred during the winter 2013-2014 (events from 24 December 2013 to the 1 March 2014) were monitored with the on-line instrumentation installed in-situ. As indicated above (section 3.1.2) the winter 2013-2014 was anomalous because of the relatively high temperature and the frequent and abundant rainfall events occurred in the monitoring area and in the whole alpine region. The use of de-icing salts was thus reduced in comparison with the amount expected to be used in “normal” winters. Furthermore, in each event of precipitation, the antecedent dry period without precipitations was particularly short, which caused limited periods of pollutant build-up on the road surface. Among all the runoff events monitored (11 events), analytical parameters (measured in lab) regarded 5 significant runoff events and the main results obtained for the quantitative and qualitative characterisation are presented and discussed in the following sections.

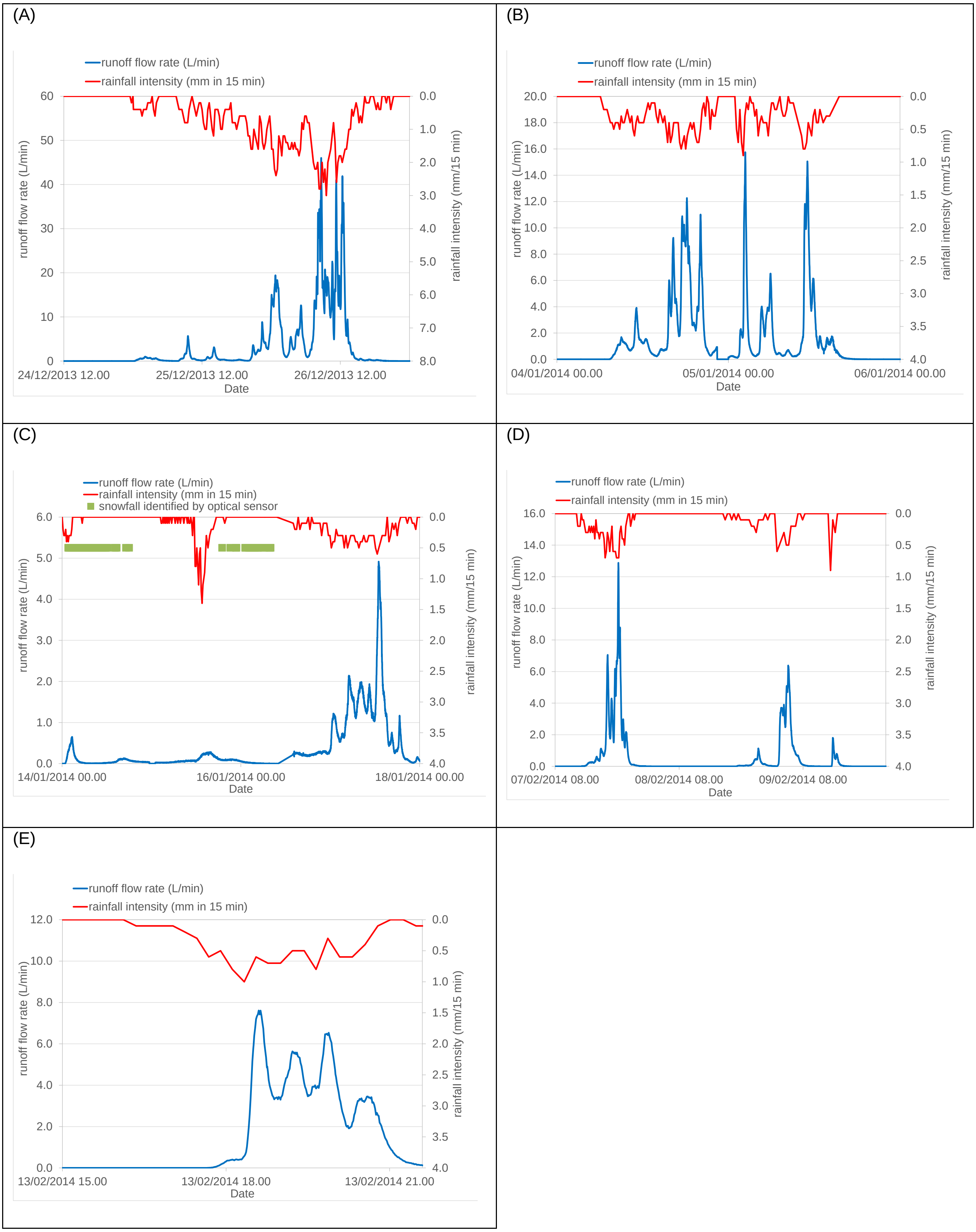


Figure 11: Data of rainfall intensity and the corresponding runoff flow rate for 5 runoff events; winter 2014/2014.

Quantitative characterisation of runoff

The diagrams of rainfall intensity over time (hyetograph) and the corresponding runoff flow rate (hydrograph) for the 5 events which were fully investigated during the winter period 2013/2014 are shown in Figure 11. All the events regard rainfall precipitation, except for the monitoring from 14/01/2014 to 18/01/2014 when also snowfall was observed (Figure 11C). Due to the small area producing runoff, the time of the peaks of the rainfall coincides with the time of the peaks of flow rate, except for the hydrograph of the event of 14/01/2014. In this case the production of runoff water was almost absent during snowfall which was indicated in green pencil in Figure 11C; however, after the end of snowfall the beginning of rainfall caused an immediate production of runoff water (Figure 11C).

Qualitative characterisation of runoff

Figure 12 shows the time profiles of the conductivity along the 5 runoff events during the winter 2013/2014. During all the runoff events, the level of contamination depended on the time: the highest conductivity was found at the beginning of the precipitation and at the beginning of runoff, whilst conductivity decreased progressively in the following part due to the progressive washout of the road surfaces. Except for the first monitoring (from 24/12/2013 to 26/12/2013), which was characterised by the lowest values of conductivity, the following runs showed very high peaks of conductivity which surpassed often 1000 microS/cm and reached occasionally 10.000 microS/cm. Concerning the influence of rainfall intensity on the removal of salinity from roads, a correlation was not observed and even events with a low rainfall intensity displays high conductivity in water samples. In fact, the peaks of conductivity were often associated with low flow rates. This behaviour is quite different from the typical behaviour expected for suspended solids and turbidity, which are transported preferably by high-intensity rainfall events which cause higher kinetic energy and more pollutants transported [14, 15].

Snowmelting can be observed in Figure 12C (in accordance with Figure 11C). In this case, the melting of snow, combined with intermittent snowfall, produced a significant conductivity in the runoff water coupled with low flow rates but with a long duration (three days). A frequent application of de-icing salts occurred during snowfall and during interim hours of clean sky and low temperatures.

The influence of rainfall duration on salt washing was minimal. The peak of salinity occurred in the first portion of the runoff event, while the total duration of the precipitation was in general not so important.

Figure 12:Data of conductivity for 5 runoff events during the winter 2013/2014 (data of runoff flow rate were included for an immediate comparison).

The results of the lab chemical analyses obtained from the water samples collected during the for 5 runoff events in the winter 2013/2014 are summarised in Table 2. Among the 28 parameters analysed, only those above the detection limit and those with significant changes during the runoff event have been indicated and discussed here. Each event was characterised by a mean concentration calculated according to EMC, presented above in section 3.2.

Events	**TSS (mg/L)**	**EC (µS/cm)**	**Cl$^-$ (mg/L)**	**SO_4^{2-} (mg/L)**	**CN$^-$ (microg/L)**	**Na$^+$ (mg/L)**	**Al (mg/L)**	**Zn (mg/L)**
Event of 24-26 December 2013								
Sample 1	20	238	61	3.3	2	39	-	-
Sample 2	23	229	57	2.9	3	38	-	-
Sample 3	11	123	27	2	<2	19	-	-
Sample 4	7	150	33	2.1	<2	24	-	-
Sample 5	7	99	20	1.8	<2	14.3	-	-
EMC	**14**	**175**	**42**	**2.5**	**2.2**	**28**	**-**	**-**
Event of 04-06 January 2014								
Sample 1	23	968	296	3.2	9	187	0.71	1.38
Sample 2	12	674	195	2.2	6	127	0.51	1
Sample 3	11	402	116	1.6	4	75	0.37	0.77
Sample 4	11	309	88	1.5	3	57	0.37	0.64
Sample 5	4	217	60	1.1	2	40	0.23	0.45
Sample 6	6	190	52	1	3	35	0.187	0.32
EMC	***9***	***324***	***93***	***1.4***	***3.5***	***61***	***0.31***	***0.57***
Event of 14-18 January 2014								
Sample 1	78	721	217	2	25	138	1.97	1.29
Sample 2	46	358	105	1.4	15	67	1.26	0.87
Sample 3	29	388	114	1.3	10	73	0.89	0.75
Sample 4	28	268	76	1.3	9	50	0.87	0.72
EMC	***42***	***425***	***125***	***1.5***	***14***	***80***	***1.18***	***0.88***
Event of 07-09 February 2014								
Sample 1	20	8170	2690	10.4	14	1660	0.28	10.3
Sample 2	17	2880	920	4.8	12	580	0.41	4
Sample 3	13	966	190	2.7	<4	184	0.44	1.83
Sample 4	14	738	209	2.2	<4	132	0.46	1.39
*Sample 5**	9	3850	1250	9.8	5	730	0.109	6
Sample 6	2	1180	340	3.5	<4	210	0.01	1.71
EMC**	***14***	***1314***	***321***	***3.1***	***5.3***	***256***	***0.43***	***2.23***
Event of 13 February 2014								
Sample 1	55	6370	2110	7.7	23	1330	1.44	10.6
Sample 2	62	1409	436	2.6	17	282	1.81	1.82
Sample 3	35	957	286	2.1	8	182	1.09	0.84
Sample 4	12	820	237	2.6	3	156	0.21	1.2
EMC	***45***	***1159***	***353***	***2.3***	***12***	***226***	***1.37***	***1.27***

*Table 2: Results of the chemical analyses in runoff water during 5 events in the winter 2013/2014. Legend: EC: electrical conductivity. *Initiation of a second rainfall event. **Calculated on the first rainfall event (samples 1,2,3,4).*

The runoff water showed very variable concentrations of all the chemical parameters over time. Analogously to the observations indicated for conductivity, there was a very fast and clear effect of rainfall on the washing of pollutants from the road. Indeed, the concentration of pollutants in the runoff water increased immediately at the beginning of rainfall as a results of the immediate washing of the ions concentrations (first samples of each event in Table 2), with a following decrease as a result of the complete washing occurred on the road (last samples of each event in Table 2). The occurrence of the phenomenon of “first flush” was verified for some pollutants: TSS, chloride, zinc. The procedure used in not described here but it was applied according to various references in the literature [9,16]. The results obtained for all the 5 events are shown in Figure 13. First flush occurs when the curve of the “dimensionless cumulative mass of pollutant” vs. the “dimensionless cumulative volume” is above the bisector (45° line). The first-flush occurred for TSS, chloride and zinc. This means that a large fraction of these pollutants is contained in the initial runoff and the peak of concentration precedes the flow peak.

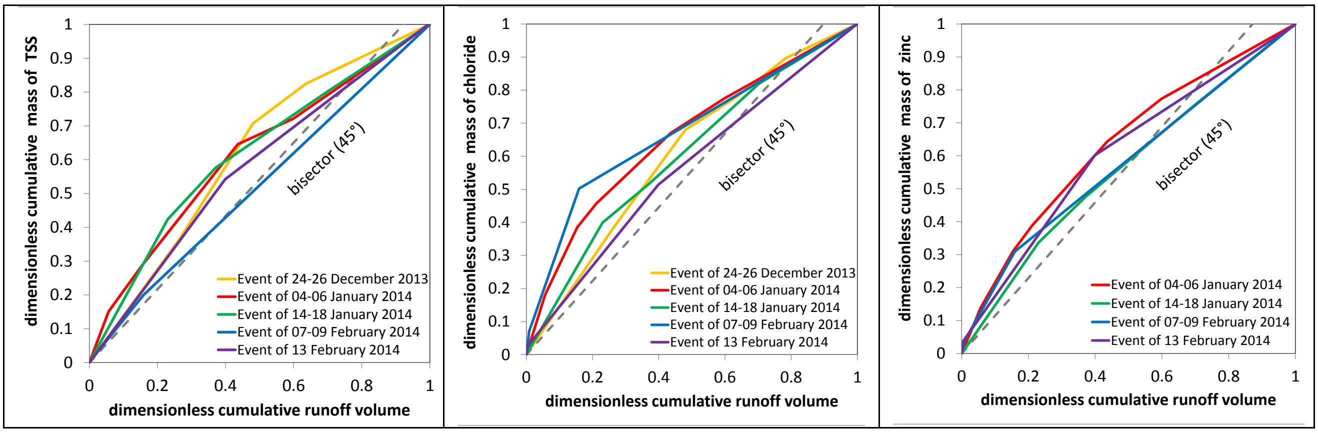


Figure 13: Assessment of “first flush” for TSS, chloride and zinc in 5 events during winter 2013/2014. First flush occurs when the curve is above the bisector (45° line).

To discuss the quality of runoff water both mean concentrations (EMC) and peak concentrations are relevant. Peak concentrations are indicated in Table 2 and are associated always with the sample 1 inside an event profile (except for some data of aluminium). Considering chloride, the EMC varied in the range 42-353 mg/L while peak was in the range 61-2690 mg/L. Analogously for electrical conductivity: EMC varied in the range 175-1314 microS/cm while peak was in the range 238-8170 microS/cm.

For a comparison, some relevant chloride standards for freshwater aquatic ecosystems are given by USEPA (2009) [17]: standards are 230 mg/L (criterion of continuous concentration and chronic toxicity) or 860 mg/L (criterion of maximum concentration and acute toxicity). This latter is relevant for short term exposures.

The data obtained in the first portion of runoff exceeded these standards, indicating a potential impact on the aquatic life, which was mitigated by the low flow rate associated to the concentration peaks (resulting in a moderate mass load).

Chloride derived from de-icing salts is soluble and thus this fraction cannot be removed by sedimentation or filtration. This a great concern in the runoff produced from roads treated with de-icing salts, because the high peaks of chloride may cause an acute impact on the receiving water bodies in the short term.

Some heavy metals (aluminium, iron) in the runoff water are in particulate form and thus related to suspended solids. In this case treatment methods such as sedimentation or filtration are in general very suitable in the removal of TSS and thus heavy metals. Conversely, zinc was present mostly in soluble form.

3.2.3. Conclusions

The runoff events due to rainfall, snowfall and melting of snow were monitored during the winter period 2013/2014 using a monitoring station equipped with a rainfall gauge, an automatic sampler, on-line sensors (conductivity, turbidity) and electronic instrumentation to record and transmit data to operators. Hydrographs and pollutographs were calculated and combined with the results of chemical analyses of 28 parameters performed in laboratory. The water quality measurements demonstrated a high intrinsic variability which was discussed observing both the Even Mean Concentration and the peak concentration for various pollutants (TSS, chloride, sulphate, sodium, cyanide, heavy metals…). The “first flush” phenomenon was observed for chloride, TSS and zinc, indicating that a large fraction of these pollutants is contained in the initial runoff. The concentration of chloride obtained in the first portion of runoff exceeded the standards for freshwaters, indicating a potential impact on the aquatic life, mitigated by the low flow rate associated to this first part of the flow.

Bibliography

[1] Rubin J., et al. (2010): “A Report by the Margaret Chase Smith Policy Center – The University of Maine”, p.37.

[2] European Commission Staff working paper SEC(2011) 207 “establishing guidelines for determination of contributions from the re-suspension of particulates following winter sanding or salting of roads under the Directive 2008/50/EC on ambient air quality and cleaner air for Europe”

[3] Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe

[4] EN 12341:1999 “Air Quality - Determination of the PM10 fraction of suspended particulate matter - Reference method and field test procedure to demonstrate reference equivalence of measurement methods”.

[5] EPA method IO-3.3, http://www.epa.gov/ttnamti1/files/ambient/inorganic/mthd-3-3.pdf

[6] EPA PMF ver. 5.0 http://www.epa.gov/heasd/research/pmf/pmf_guidelines.html

[7] Liu A., Egodawatta P., Guan Y., Goonetilleke A. (2013) Influence of rainfall and catchment characteristics on urban stormwater quality. Science of the Total Environment, 444: 255–262.

[8] Park M-H., Swamikannu X., Stenstrom M.K. (2009) Accuracy and precision of the volume-concentration method for urban stormwater modeling. Water Research, 43: 2773-2786.

[9] Lee J.H., Bang K.W., Ketchum L.H., Choe J.S., Yue M.J. (2002) First flush analysis of urban storm runoff. The Science of the Total Environment, 293: 163–175.

[10] Barbosa A.E., Fernandes J.N., David L.M. (2012) Key issues for sustainable urban stormwater management. Water Research, 46: 6787-6798.

[11] APHA (2012) Standard Methods for the Examination of Water and Wastewater, 2540 D, APHA, AWWA, WERF, 22nd ed., Washington, DC.

[12] ISTISAN (2007). ISS- Metodi analitici di riferimento per le acque destinate al consumo umano ai sensi del DL.vo 31/2001. Metodi chimici. Editors Ottaviani M. and Bonadonna L. Rapporto ISTISAN 07/31. In Italian.

[13] APAT CNR-IRSA. Rapporti 29/2003. Metodi analitici per le acque. Volumi Primo e Secondo. ISBN 88-448-0083-7. In Italian.

[14] Liu A., Egodawatta P., Guan Y., Goonetilleke A. (2013) Influence of rainfall and catchment characteristics on urban stormwater quality. Science of the Total Environment, 444: 255–262.

[15] Sansalone J.J., Koran J.M., Buchberger S.G., Smithson J.A. (1997) Partitioning and first flush of metals and solids in urban highway runoff. Journal of Environmental Engineering, 123(2): 134–143.

[16] Hvitved-Jacobsen T., Vollertsen J., Nielsen A.H. (2010) Urban and Highway Stormwater Pollution: Concepts and Engineering. CRC Press, Taylor & Francis Group. Boca Raton, New York, London.

[17] USEPA (2009) National recommended water quality criteria. US Environmental Protection Agency, Washington DC. Online at: http://www.epa.gov/waterscience/criteria/wqctable/.