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Implementation of an active 'bryomonitoring' network for chemical status and temporal trend assessment under the Water Framework Directive in the Chiampo Valley's tannery district (NE Italy)

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ABSTRACT

An innovative network based on transplanted bryophytes providing a continuous monitoring of the priority substances Cd, Hg, Ni, and Pb and other trace elements (Co, Cr, Cu, Fe, Mn, Zn) was designed for the watercourses flowing across an industrial district of NE Italy where both permitted and illegal wastes cause sporadic, intermittent or chronic events of environmental alteration. During a two-year preliminary survey, over 300 biomonitoring actions ('moss bag' transplantation and recovery) were successfully carried out at 25 stations: 190 of them occurred under acceptable conditions and provided results suitable for comparisons. Five environmental priorities were assessed and characterized in space and time. For these situations local authorities drafted a protocol for data management, to plan official controls and dissuasive actions. The 'moss bag' technique allows a flexible approach for both surveillance monitoring (trend assessment) and investigations (point source detection) in compliance with the Water Framework Directive 2000/60/EC as suggested by the recent Guidance Document on chemical monitoring of sediment and biota.

1. Introduction

Metals and metalloids derive from natural processes of mineral dissolution, atmospheric deposition and gaseous exchanges, but their concentrations in the environment have increased more and more in the last decades, as a consequence of human activities: domestic, industrial and mining effluents, agriculture, livestock farming. Human pathologies directly or indirectly caused by trace elements show an increasing trend: As, Be, Cd, Cr(VI), Ni, and probably Pb are carcinogenic for man (I.A.R.C., 2010). Water and food may transfer many toxic substances from the environment to human beings and despite progress in purifying technologies, metals are persistent and still represent a menace for health (W.H.O., 2007).

1.1. Water Framework Directive

The 'Water Framework Directive (W.F.D.) 2000/60/EC' (European Parliament and Council, 2000) aims to achieve a good quality status for surface, ground and coastal waters throughout Europe by 2015. It is also expected to contribute to the protection, prevention of deterioration and improvement of all water bodies across the European Union. Water quality status is to be monitored by the use of I) biological, II) hydro-morphological and III) chemical/physico-chemical indicators, which must be in compliance with specific Environmental Quality Standards (E.Q.S.). For chemical monitoring, the W.F.D. provided a list of 33 'Priority Substances' (P.S.) including four metals: Cd, Hg, Ni and Pb. Twelve of these substances (e.g. Cd and Hg) are presently indicated as 'Priority Hazardous Substances' (P.H.S.), subjected to the cessation or phasing out of discharges, emissions and losses in 20 years (European Commission, 2000).

The W.F.D. does not mandate the use of a particular set of methods and spot sampling is currently the most commonly used method for measuring levels of chemical pollutants. However, this method provides only point results gathered at the instant of sampling and could prevent the assessment of episodic or

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intermittent events, when concentrations widely fluctuate in space and time. Greenwood and Roig (2006) recently created a directory of screening tools, 'SWIFT-WFD', for chemical and ecological status monitoring under the 2000/60/EC. Three monitoring issues are discussed: A) physico-chemical assessment tools, B) chemical assessment techniques, and C) biological assessment techniques, including bioindicators (systematic or ecological approach) and sentinel organisms (bioaccumulators, e.g. mussels).

1.2. Chemical monitoring under the WFD

The recent Guidance Document No. 25 on chemical monitoring of sediment and biota under the W.F.D. (European Parliament and Council, 2010) ascribes a renewed importance to the analysis of accumulators, which is correctly considered a cost-effective approach to compare contaminant concentrations in different areas and to identify pollution sources. In using sediment and biota as a first level screening for certain chemicals in the monitoring programme, water measurements may be downscaled.

Directive 2008/105/EC (European Parliament and Council, 2008) defines the 'good chemical status' to be achieved by all Member States in 2015 and gives, together with the W.F.D., the legal basis for the monitoring of priority substances in sediment and biota. As the Guidance Document No. 27 (European Parliament and Council, 2011) indicates, substance concentrations in biological or non-biological accumulators could be converted into their concentration in water by use of specific Bio-Concentration/Bio-Accumulation Factors, for E.Q.S. derivation at local level (Babut et al., 2003).

One of the most successful bioaccumulation techniques is that based on aquatic bryophytes, native or transplanted, whose intense and widespread deployment in several European watercourses since the 1970's (Besse et al., 2012; Burton, 1990; Tyler, 1990) is very promising for both surveillance and investigative monitoring, even in aggressive environments such as effluents (Figueira and Ribeiro, 2005; Mersch and Reichard, 1998). A recent study carried out by Divis et al. (2006) proved that the concentrations of Cd, Pb, Cr and Zn measured using D.G.T. (passive samplers) correspond well with those obtained after the deployment of *Fontinalis antipyretica* transplanted along the same watercourse.

In the last decades, several authors established regional background levels of trace elements for native aquatic bryophytes in Northern England, Belgium and France (Mouvet, 1986; Mersch and Claveri, 1998), Galicia – Spain (Carballeira and Lopez, 1997), Swiss Alps (Samecka-Cymerman and Kempers, 1998), Sudety Mountains – Poland (Samecka-Cymerman et al., 2007) and Maritsa River – Bulgaria (Gecheva et al., 2011). The same goal have been recently gathered by means of transplanted bryophytes (moss bags) in the Bacchiglione River Basin, NE Italy (Cesa et al., 2010). Background calculation is fundamental for the calibration of new environmental pollution indices and a river basin approach must be followed, since element concentrations in water and mosses could depend on substrate lithology.

In the process of developing a monitoring strategy for biota it is crucial to consider the importance of Environmental Specimen Banking (E.S.B.), the collection and storage of biota for real-time monitoring, retrospective monitoring and ecotoxicological research. An E.S.B. approach based on aquatic bryophytes has been recently adopted for Galicia (NW Spain) by the University of Santiago de Compostela (Vazquez et al., 2007).

1.3. Aims and objectives of the present work

In NE Italy a biomonitoring network was requested by Giada Agency, a public body which is charged of coordinating an integrated environmental administration in a tannery district with the aim of preserving ecosystem integrity and equilibrium, for a global life quality improvement. The project involves the Regional Agency for Environmental Protection (A.R.P.A.V.) and has the following main objectives:

1. Design of a preliminary biomonitoring network for the survey area;
2. Test of materials/methods and assessment of logistical/technical constraints in the field;
3. Characterization of trace element pollution in watercourses;
4. Investigation of point sources and warning of authorities;
5. Implementation of the final biomonitoring network.

This paper aims at I) reporting the implementation phases of an original biomonitoring network and II) showing the suitability of moss bags for detecting and investigating point sources of trace element pollution.

As far as we know, this is the first example of a biomonitoring network based on the exclusive deployment of transplanted bryophytes.

2. Materials and methods

2.1. Design of the network and time-sheet of the implementation phases

The preliminary network (objective No. 1 of the project, Table 1) including 16 permanent stations was designed by Giada Agency on the basis of expertise in the environmental risks of this territory. The network was implemented in 3 phases:

Phase 1) The period from June 2009 to January 2010 was exclusively devoted to assess logistical/technical constraints of biomonitoring activities in the field (objective No. 2 of the project) and to characterize trace element pollution in space and time (objective No. 3).
Phase 2) Investigations on the main pollution events (objective No. 4) started in February 2010 and required the activation of 9 additional stations. Data collection stopped in September 2011.
Phase 3) The results achieved during the two-year experimentation were exploited to design the final biomonitoring network (objective No. 5), which was activated in April 2011.

2.2. Survey area

The Chiampo Valley's tannery district is located on the border between the provinces of Vicenza and Verona (Veneto Region, NE Italy) and is characterized by bovine leather manufacturing used almost exclusively in the furniture, shoe and clothing industries. The district absorbs 50% of the leather manufactured in Italy. Major pollution risks for aquatic environment derive from waste water purification plants, urban and special waste dumps and factories whose effluents are directly discharged in surface waters. In general, the land use is promiscuous and watercourses exploited for agricultural purposes are also the waster bodies receiving urban and industrial wastes. Furthermore, most of the Venetian plain is an important groundwater recharge area. For these reasons, the monitoring of priority substances in the Chiampo Valley may contribute to preserve human health.

Three watercourses flow across the tannery district and were surveyed (Table 1, Fig. 1): River Chiampo, belonging to the Adige river basin, and Rivers Agno-Guà and Rio Acquetta, belonging to the Agno-Gorzone river basin. Both basins are pluvial-nival systems