Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Development of a powerful approach for classification of surface waters by geochemical signature

Montserrat Filella [a,*], Ian Pomian-Srzednicki [b], Pascale M. Nirel [c]

[a] Institute F.-A. Forel, University of Geneva, Route de Suisse 10, CH-1290 Versoix, Switzerland
[b] Rue du Gothard 2, CH-1225 Chêne-Bourg, Switzerland
[c] Service de l'écologie de l'eau, Av. Sainte-Clotilde 23, CH-1211 Geneva 8, Switzerland

ARTICLE INFO

Article history:
Received 18 June 2013
Received in revised form
25 November 2013
Accepted 28 November 2013
Available online 7 December 2013

Keywords:
Rivers
Chemical signature
Water classification
Geology
Uranium
Barium

ABSTRACT

Easy identification of chemical signatures characteristic of water systems has become a major issue in the field of environmental protection and management. We propose an exploratory method, exclusively based on the statistical analysis of river water composition, capable of characterizing river waters in a given watershed through their chemical composition, as well as of detecting modifications, even when not related to pollution sources. Although the method is based on well-known statistic techniques (Principal Component Analysis and Linear Discriminant Analysis), and therefore is very simple and straightforward to apply, it goes far beyond the common data reduction use of these techniques. Its capabilities are illustrated through its application to rivers in Canton Geneva, Switzerland, a hydrographical network consisting of 310 km of waterways with 250 streams and rivers. The procedure results in a very satisfactory classification of watersheds, in our case by using only two geochemical indicators: U and Ba concentrations. The method also makes it possible to follow the seasonal evolution of river regimes or the effect of wetlands on river water composition.

1. Introduction

It is widely-accepted that knowledge of the 'natural' chemistry of surface waters is fundamental to identifying substances associated with pollution (Menzi et al., 2009). Moreover, current legislation on water bodies (e.g. the European Water Framework Directive (European Union, 2000), Swiss LEau (Swiss Confederation, 1991)) emphasizes the need for a "good chemical status" in order to achieve the desired "good ecological status". Since current legislation is mostly based on River Basin Management Planning, catchment management plans are required to address these questions in each catchment. In practice, this means that the possibility of easily identifying the chemical signature characteristic of a water system has become a major issue with significant impact in the field of protection and management of our environment.

Although water chemical composition results from multiple factors (i.e., atmospheric, geological, biological, etc.), in the absence of anthropogenic pollution, geology is the main supplier of water components. The chemical signature of geological origin mainly originates in the interactions

* Corresponding author.
E-mail address: montserrat.filella@unige.ch (M. Filella).

0043-1354/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.watres.2013.11.046

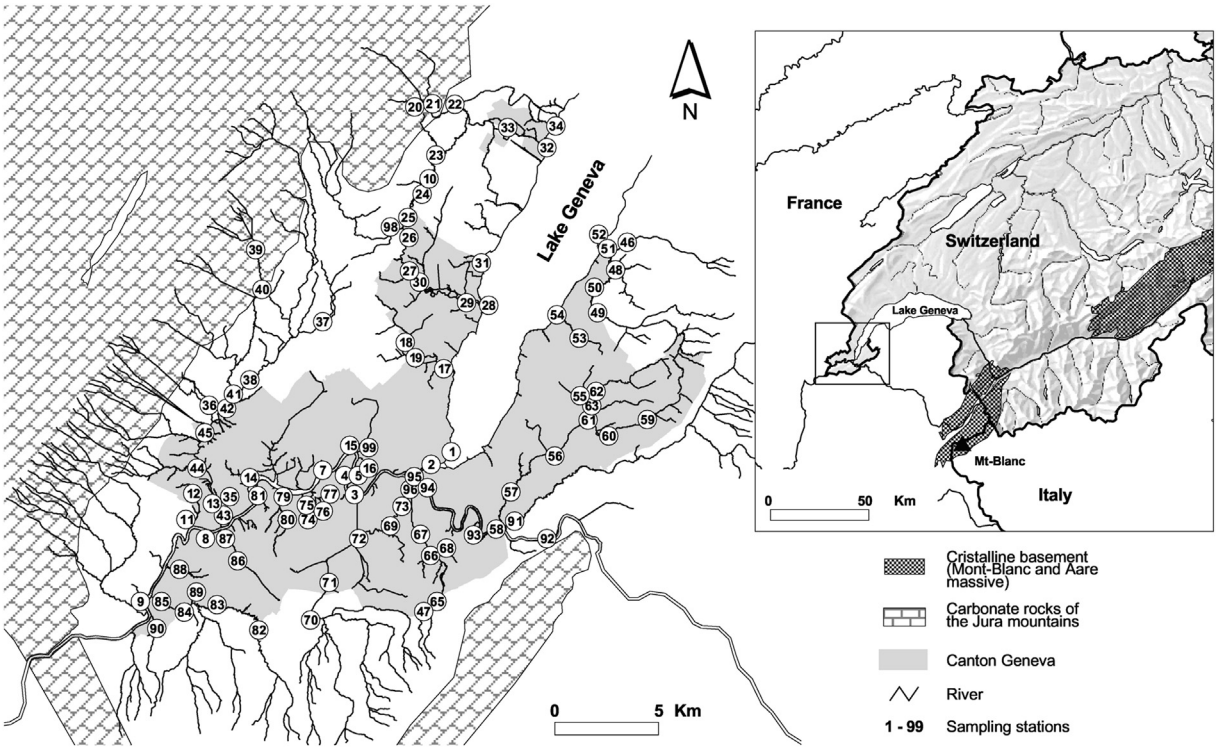

Fig. 1 – Simplified geological map of the Geneva canton with location of sampling sites. A detailed list of sampling sites can be found in Table S3.

between water, soil and subsoil (Drever, 1997) and, in practice, identifying it is far from straightforward because of the many confounding factors. Indeed, the processes controlling the chemical composition of a given water body are dependent on both bioclimatic variables (e.g., temperature, frequency and amplitude of rainfall, type and abundance of microflora) and properties of the physical environment (e.g., porosity, hydraulic conductivity) (Garrels and Mackenzie, 1967; Meybeck, 1987).

Here we propose a method exclusively based on the statistical analysis of river water composition which is able to classify river waters in a given watershed through their chemical composition. The method is explained by applying it to rivers in Canton Geneva, Switzerland. These rivers are an ideal test system because they are in contact with a wide range of terrains with contrasting geochemical, hydrological and structural properties. Although statistical tools, such as Principal Component Analysis (PCA), have been extensively used in the environmental sciences, they have been mostly used for data reduction purposes only. Here we propose a new methodological approach that, on the basis of these techniques, allows the easy and robust classification and follow-up of water bodies without the need of performing endless and expensive analysis. This approach is a powerful tool for the characterization of watersheds according to their hydrological and ecological region mandatory under the above-mentioned legislation (Omernik, 2004; Menzi et al., 2009).

Table 1 – Description of sites studied.

Type	Number of streams	Number of sampling sites	Number of samples
Alps	2	11	452 (22%)
Jura	16	30	804 (40%)
Plain	19	31	598 (29%)
Wetland	7	17	175 (9%)
Total	44	89	2029

2. Materials and methods

2.1. Sites studied

The hydrographical network of the Geneva area consists of 310 km of waterways, comprising 250 streams and rivers. The major watercourse, and final collector for all waters, is the Rhone River. The sources of all the streams, with the single exception of the Seymaz, are outside the canton, for the most part in neighbouring France. The vast majority of the streams (196) are less than 1 km long. The surface area of the Canton of Geneva (282 km^2) is primarily devoted to agriculture (40%), buildings (33%) and woodland (12%), with the remaining area being occupied by the lake and surface waters (14%) and miscellaneous uses (1%) (République et Canton de Genève, 2012).

The geological features of the Canton of Geneva also vary considerably (Wildi and Pugin, 1998; www.toposhop.admin.ch/fr/shop/products/maps/geology/gk500/vector_1#). Located at the south-western tip of Lake Geneva, it is formed by a drainage basin surrounded by the Jura and Alps mountain ranges (Fig. 1). Waters flowing in Canton Geneva are