Environmental Research 134 (2014) 410–419

Contents lists available at ScienceDirect

Environmental Research

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

Impact of trace metals from past mining on the aquatic ecosystem: A multi-proxy approach in the Morvan (France)

E. Camizuli [a,*], F. Monna [a], R. Scheifler [b], P. Amiotte-Suchet [c], R. Losno [d], P. Beis [a], B. Bohard [a], C. Chateau [e], P. Alibert [c]

[a] UMR 6298, ARTéHIS, Université de Bourgogne—CNRS-culture, Boulevard Gabriel, Bat. Gabriel, 21000 Dijon, France
[b] UMR 6249, Chrono-Environnement, Université de Franche-Comté—CNRS, Place Leclerc, 25000 Besançon, France
[c] UMR 6282, Biogeosciences, Université de Bourgogne—CNRS, Boulevard Gabriel, Bat. Gabriel, 21000 Dijon, France
[d] UMR 7583, LISA, Universités Paris 7-Paris 12—CNRS, 61 avenue du Gal de Gaulle, 94010 Créteil Cedex, France
[e] Université de Bourgogne, UFR SVTE, Bat. Gabriel, 21000 Dijon, France

ARTICLE INFO

Article history:
Received 1 April 2014
Received in revised form
9 July 2014
Accepted 16 July 2014
Available online 27 September 2014

Keywords:
Bioaccumulation
Body condition index
Wild brown trout
Streambed sediment
Bryophyte
Fluctuating asymmetry

ABSTRACT

This study seeks to determine to what extent trace metals resulting from past mining activities are transferred to the aquatic ecosystem, and whether such trace metals still exert deleterious effects on biota. Concentrations of Cd, Cu, Pb and Zn were measured in streambed sediments, transplanted bryophytes and wild brown trout. This study was conducted at two scales: (i) the entire Morvan Regional Nature Park and (ii) three small watersheds selected for their degree of contamination, based on the presence or absence of past mining sites. The overall quality of streambed sediments was assessed using Sediment Quality Indices (SQIs). According to these standard guidelines, more than 96% of the sediments sampled should not represent a threat to biota. Nonetheless, in watersheds where past mining occurred, SQIs are significantly lower. Transplanted bryophytes at these sites consistently present higher trace metal concentrations. For wild brown trout, the scaled mass and liver indices appear to be negatively correlated with liver Pb concentrations, but there are no obvious relationships between past mining and liver metal concentrations or the developmental instability of specimens. Although the impact of past mining and metallurgical works is apparently not as strong as that usually observed in modern mining sites, it is still traceable. For this reason, past mining sites should be monitored, particularly in protected areas erroneously thought to be free of anthropogenic contamination.

1. Introduction

Trace metals (TMs) persist in the environment, reaching potentially toxic levels for biota over time (Linde et al., 1998; Alibabić et al., 2007). Elevated TM concentrations may result from human activity (e.g. emissions from urban and industrial areas), and also from the natural weathering of metal-enriched rocks and ore bodies (Aleksander-Kwaterczak and Helios-Rybicka, 2008). In the case of mining, both natural and anthropogenic factors are involved; mineral deposits correspond to anomalous areas, while their exploitation may considerably extend metal dispersal. Mining and smelting activities often continue to affect the environment, even centuries after such sites have been abandoned (Casiot et al., 2009). River systems naturally drain mining waste (workshop grounds, slag heaps, and cleansing dumps), mobilising TMs by physical or chemical processes, and thus contaminating aquatic ecosystems for centuries, or even millennia (Miller, 1997). The first step in understanding how past mining still impacts ecosystems is by characterising TM geographic distribution (Deacon and Stephens, 1998). Trace metals may spread far from their place of origin under certain hydrological conditions (Audry et al., 2010). Analysing water chemistry is not completely satisfactory because water composition is affected by meteorological conditions. Streambed sediments are not true permanent sinks, but they do record the composite erosion products of terrains in the catchment area, including mines located upstream (Elbaz-Poulichet et al., 2011). Complex chemical procedures have been developed to approximate TM bioavailability (Gismera et al., 2004; Leleyter et al., 2012), but bioindicators have proved more valuable to assess environmental impacts, because they accumulate TMs over time (Bleuel et al., 2005). Two categories of bioindicators can be distinguished: sessile organisms yield information about contamination at the place where they live, while mobile organisms record contamination over a larger area (Cenci, 2000). Aquatic bryophytes, such as *Fontinalis antipyretica*, belong to the first category. They present several characteristics that make them

* Corresponding author. Tel: +33 (0)3 80 39 36 26; fax: +33 (0)3 80 39 57 87.
E-mail address: estelle.camizuli@u-bourgogne.fr (E. Camizuli).

http://dx.doi.org/10.1016/j.envres.2014.07.008
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suitable for monitoring studies (Bruns et al., 1997; Vázquez et al., 2004; Samecka-Cymerman et al., 2005): (i) they are essential members of food webs (Bleuel et al., 2005), and (ii) their cuticles are permeable to water, so that metals integrate their tissues by leaf surface and not by roots (Figueira and Ribeiro, 2005). These plants accumulate metals at levels several orders of magnitude higher than the water in which they live (Martins and Boaventura, 2002). Researchers have developed the so-called moss bag technique, which possesses the advantage of using a single species, with an adequate amount of material whatever the targeted site. Above all, time of exposure can be controlled precisely, making the interpretation of metal contents easier (Cesa et al., 2006). The wild brown trout (*Salmo trutta Fario*) belongs to the mobile category (up to ten kilometres, in our rivers, pers. comm. P. Berrebi). It is widely used as a sentinel species to monitor aquatic environments (Linde et al., 1998; Foata et al., 2009; Allenbach, 2011). This widespread predatory fish is situated at the top of the food web. Studies have already been undertaken on its tissues, providing a basis for comparison (Has-Schön et al., 2008; Monna et al., 2011). Fish liver is generally considered to be one of the best indicators of chronic exposure to TMs, because of its role in the accumulation, transformation and excretion of contaminants (Linde et al., 1998).

The present study focuses on the Morvan region. Today, this area is one of the least inhabited regions in France. It has nonetheless experienced several phases of mining and smelting of non-ferrous metals since at least the Bronze Age (Monna et al., 2004; Jouffroy-Bapicot et al., 2007). Even though no mining activity continued after the 20th century, mining may nevertheless have caused persistent local TM contamination. A sediment quality index (SQI; see Marvin et al. (2004) for details) was computed from TM concentrations (i.e. As, Cd, Cr, Cu, Ni, Pb and Zn) measured by the French Geological Survey (BRGM) in streambed sediments, to find new mineral deposits. After the SQI map had been used to provide a general overview of the Morvan, the map was combined with archaeological data to select three specific watersheds, differently affected by past mining (low, medium, and high contamination). For each watershed, four commonly investigated trace elements were studied: Cu and Zn (essential), and Cd and Pb (non-essential). Concentrations were measured in transplanted aquatic mosses (*F. antipyretica*) sampled twice, a month apart. Liver Cd, Cu, Pb and Zn concentrations were also measured in wild brown trout (*S. trutta*), caught at the same sites. Body condition indices were calculated, as they are well-known indicators of organism health (Peig and Green, 2010). Fluctuating asymmetry (FA) was measured on four bilateral traits, and used to quantify stress in wild brown trout (e.g. Sanchez-Galan et al., 1998; Monna et al., 2011). Higher degrees of asymmetry are expected in cases of strong environmental stress during early development (Allenbach, 2011). Such a scheme, where TM levels are measured in both abiotic and biotic compartments at the same sites, is suitable to assess metal transfers in ecosystems and their possible deleterious effects (Deacon and Stephens, 1998).

2. Materials and methods

2.1. Study area

2.1.1. The Morvan

The Morvan Regional Nature Park (MRNP) is a protected area (since 1970), situated in the north-eastern Massif Central, France (Fig. 1a). It covers 2814 km^2, for a population of just over 70,000 inhabitants (Fig. 1b). Industries are very scarce, and

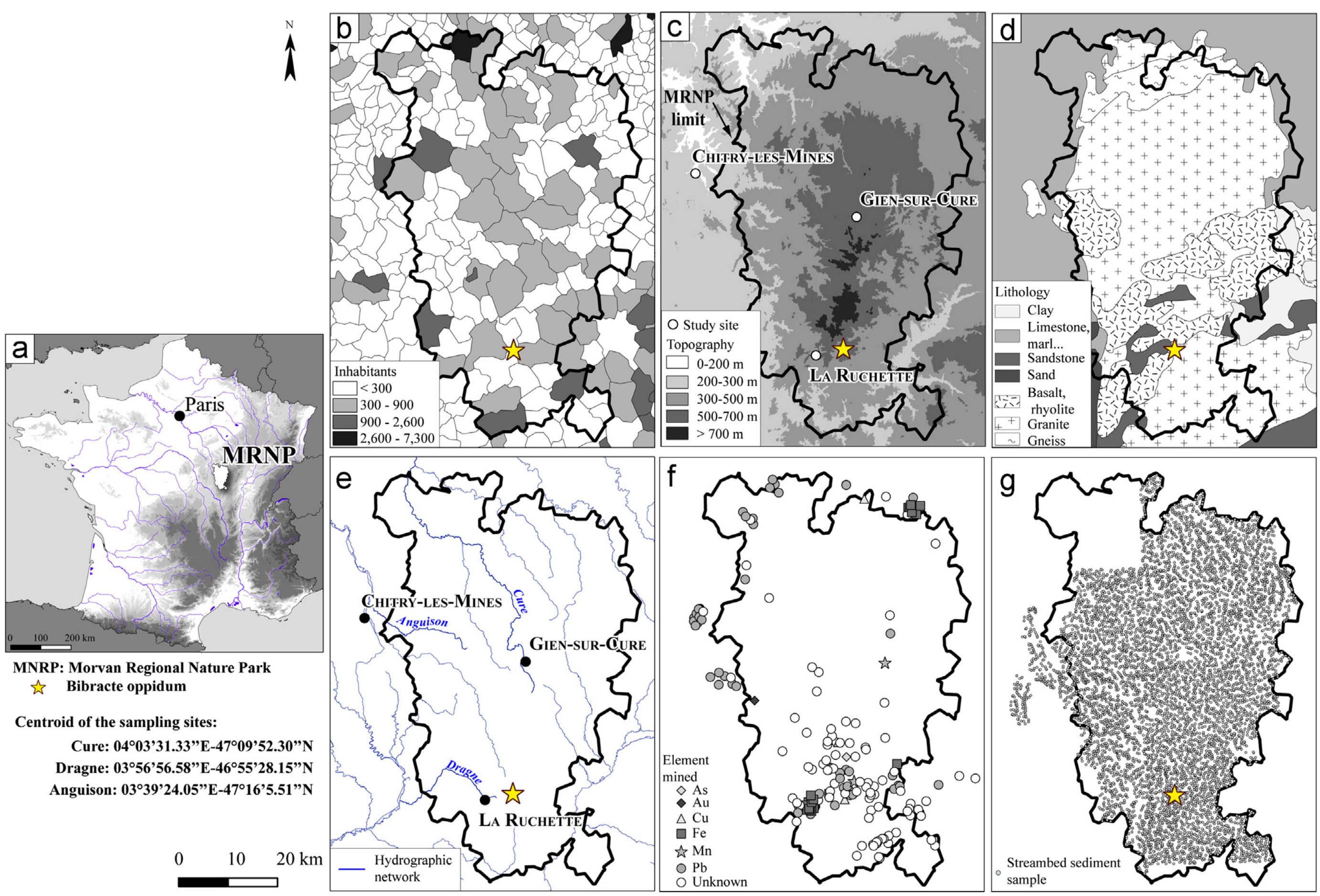

Fig. 1. (a) location of the MRNP in France, (b) numbers of inhabitants in Morvan localities, (c) digitalised elevation model, (d) lithological map, (e) simplified hydrographical network, (f) map of the mining sites, for which the nature of minerals exploited is indicated when known, (g) BRGM sampling location for streambed sediments.