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# Bivalve mollusks in metal pollution studies: From bioaccumulation to biomonitoring

Michael Zuykov<sup>a,\*</sup>, Emilien Pelletier<sup>a</sup>, David A.T. Harper<sup>b</sup>

<sup>a</sup> Institute des sciences de la mer de Rimouski (ISMER), Université du Québec à Rimouski, Rimouski, 310, allée des Ursulines, QC, Canada G5L 3A1 <sup>b</sup> Department of Earth Sciences, Durham University, Durham DH1 3LE, UK

#### HIGHLIGHTS

• Bivalve mollusks are good applicable in metal monitoring studies.

• No drastic effects of accumulated metals on the health of bivalves were documented.

Shells cannot be reliable used for reconstruction of the pollution history.

• Biomarkers provide common information about unfavorable environmental conditions.

• Biomonitoring of metal pollution using bivalves is not far advanced.

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#### ABSTRACT

Contemporary environmental challenges have emphasized the need to critically assess the use of bivalve mollusks in chemical monitoring (identification and quantification of pollutants) and biomonitoring (estimation of environmental quality). Many authors, however, have considered these approaches within a single context, i.e., as a means of chemical (e.g. metal) monitoring. Bivalves are able to accumulate substantial amounts of metals from ambient water, but evidence for the drastic effects of accumulated metals (e.g. as a TBT-induced shell deformation and imposex) on the health of bivalves has not been documented. Metal bioaccumulation is a key tool in biomonitoring; bioavailability, bioaccumulation, and toxicity of various metals in relation to bivalves are described in some detail including the development of biodynamic metal bioaccumulation model. Measuring metal in the whole-body or the tissue of bivalves themselves does not accurately represent true contamination levels in the environment; these data are critical for our understanding of contaminant trends at sampling sites. Only rarely has metal bioaccumulation been considered in combination with data on metal concentrations in parts of the ecosystem, observation of biomarkers and environmental parameters. Sclerochemistry is in its infancy and cannot be reliably used to provide insights into the pollution history recorded in shells. Alteration processes and mineral crystallization on the inner shell surface are presented here as a perspective tool for environmental studies.

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\* Corresponding author. Tel.: +1 418 732 8357; fax: +1 418 724 1842. *E-mail addresses*: michael.zuykov@yahoo.com, m.zuykov@mail.ru (M. Zuykov).

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#### 1. Introduction

A recent review (Gupta and Singh, 2011) and two papers (Boening, 1999; Waykar and Deshmukh, 2012) have the almost identical titles of "an evaluation of bivalve mollusks as biomonitors of metal pollution"; moreover related chapters in several comprehensive reviews (e.g. Philips, 1977, 1980; Zhou et al., 2008) have been dedicated to this theme. These studies provide in depth discussion on metal bioaccumulation and metal bioavailability, highlighting the historical usage of bivalves in environmental studies. Put very simply, chemicals present at undetectable levels in water can be identified in bivalves due to their high bioaccumulation ability. This idea, being one of the basic principles of the biogeochemistry (as a field of science) originally proposed by the Russian academician V.I. Vernadsky at the beginning of 20th century, was successfully implemented in the simple and cost effective 'Mussel Watch' monitoring scheme, promoted by Goldberg (1975). In particular, this approach involved the bulk analysis of metals in the soft tissues/ shells of bivalves (Koide et al., 1982; Farrington et al., 1983). Thus, bivalves were used as organisms from the field that accumulate metals in tissues; this corresponds to the definition of a biological monitor (biomonitor) provided by many authors (see Phillips and Rainbow, 1993; Luoma et al., 2009). Currently, the bibliographic database Scopus provides information on more than five hundreds papers dealing with the measurement of metal concentrations in bivalves collected from natural environment or those obtained after laboratory experiments; such scientific activity will continue. These studies have formed the common assumption that bivalves have a significant potential as useful biomonitors for metal monitoring. However, metal concentrations show enormous variability across metals and all invertebrates at generic and even at specific levels (Rainbow, 2002). Hence, it is impossible to determine contamination levels in an aquatic ecosystem directly, using only metal bioaccumulation data in bivalves because they are influenced by a number of biotic and abiotic factors. Furthermore, due to a depuration effect, the residence time of the pollutant may be shorter than the time interval separating two sampling periods (Freitas et al., 2012). Searching for the link between bioaccumulated metals and their toxicity effects in aquatic invertebrates, as well as development of biodynamic models (how and why metal bioaccumulation differs among metals, species, and environments) are currently ongoing research themes (Luoma and Rainbow, 2005; Bourgeault et al., 2011; Rainbow and Luoma, 2011). However, using biodynamic models to predict metal bioaccumulation requires knowledge of various kinetic and physiological parameters that are usually determined experimentally. Thus, recently Adams et al. (2011) noted: "However, despite their clear advantages, even these models do not fully reflect the true complexity of a real environment in which different exposure routes, conditions, and organisms have to be considered". In other words, this suggests that an objective statistical model, for use in the field, that explicitly links a concentration of metals in bivalves to changes in aquatic ecosystem health (e.g. the effects on population and communities) is not yet theoretically possible. Significantly, to date, evidence for the drastic effects (shell deformations, imposex, etc.) of accumulated metals on bivalve health has not been documented even for heavily polluted industrial sites (mine, harbors, etc.) including sites in Ukraine and Russia, highly contaminated with radionuclides (Zuykov et al., 2011a); this, however, does not seek to discuss genotoxic and cytotoxic effects (i.e. biomarker approach). In

contrast to metal contaminants, the effects of organic contaminants at individual, population and community-level is apparently visible in case of aquatic organisms. For instance, Zasypkina (2006) noted significant shell abnormalities (sinistrality and scalarity) in pulmonate gastropods, abnormal egg clusters (duplex egg capsules, embryos of irregular shape and lesser size), a low taxonomic diversity in the gastropod fauna (eight species, in comparison with neighboring water communities with >100 species) from the Lake Kara-Khole (Russia) contaminated by toxic rocket fuel related to the spaceship activities of the Baikonur cosmodrome (Kazakhstan). In this case (and in the other cases), however, laboratorial experiments should be carried out to provide a direct effect of contaminant. Finally, the different monitoring approaches such as, metal monitoring and biomonitoring have been synonymized in many papers and to date their relationships have never been unraveled and critically assessed.

New environmental challenges, such as the metal engineered nanomaterials, which are developing at an accelerated rate, and their imminent introduction into various environmental compartments have prompted the need to revisit the use of bivalves in a range of metal pollution studies. The study of lethal concentrations and other related toxicological tests with bivalves (including larvae), as well as distinct biomarker reactions, are excluded from the present discussion. Our specific goals are: (1) to clarify uncertainties of using the term 'biomonitoring' that is currently widespread in ecological literature on bivalves, (2) to discuss the use of the soft tissues and shells of bivalves in metal monitoring and biomonitoring of environmental quality (health), and (3) to show that observation of the internal shell surface with scanning electron microscope (SEM) may provide additional information for monitoring metal pollution in aquatic environments.

#### 2. Remarks on terminology

As noted by many authors (see Phillips and Rainbow, 1993), the fact is that many of the key terms used in studies of environmental pollution are broad in nature, and some of them (in fact quiet distinct) have been erroneously synonymized or used improperly. In the last book, in particular, useful discussion of the terms "biological indicator", "biological monitor", "trace metals" and "heavy metals" has been included. Further confusion exists with respect to the terminology employed for the identification and quantification of metals removed from ambient water by bivalve mollusks, that is a widely used technique in environmental studies. It has been referred not only as metal bioaccumulation studies or metal monitoring, but also the biomonitoring of metals (e.g., Lionetto et al., 2001; Duquesne and Riddle, 2002; Conti and Cecchetti, 2003; Tomazelli et al., 2003; Wagner and Boman, 2004; Kljaković-Gašpić et al., 2006, 2007; Maanan, 2007; Abdallah and Abdallah, 2008; Sarkar et al., 2008; Moschino et al., 2011; Yap et al., 2011; Langston et al., 2012). For example, Zhou et al. (2008, p. 139) noted in their recent review: "Lots of bivalve mollusks have been adopted in the biomonitoring of metal pollution in aquatic ecosystem. Exemplary bivalve mollusks include mussel, oyster, clam, etc. Bioaccumulation is the common used means in biomonitoring using this species." The 'quantitative concept' of biomonitoring has been defined and discussed in many papers, e.g., by Langston et al. (2012, p. 292): "Biomonitoring is a valuable addition to the tools used to gauge contamination (water quality analysis, toxicity testing and ecological survey) because it provides

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