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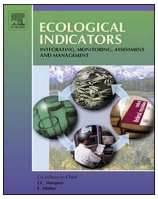

Original Articles

Fluorine and metals in *Polygonum arenastrum* Bor. from areas influenced by various types of industry

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ABSTRACT

A herbaceous plant *Polygonum arenastrum* Bor. (= *P. aequele* Lindm., *Polygonum aviculare* ssp. *aequale* (Lindman) Ascherson & Graebner) (equal-leaved knotgrass), is a widespread, good coloniser, able to survive in wastelands where other species became extinct. Therefore, the bioindication abilities of this species for F, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn were investigated. *P.arenastrum* was collected from 90 sites affected by six polluting factories: copper smelter, chlor-alkali plant, former ferrous-chromium smelter and active combustion smelter, power plant, cement plant and coke plant. Plant samples were collected at 0.75, 1.5, 3 and 4.5 km from each of these polluters in N, S, W and E directions. For comparison, a control site with 16 sampling points was selected in an area relatively free from pollution. Concentrations of Cr, Cu, Fe, Pb and Zn in shoots and roots positively correlated with those in soil (both total and plant-available). Cu, Pb and Zn in *P.arenastrum* were within the values reported in literature as toxic for other plants with the highest bioaccumulation factor (BF) from soil to shoots for Cr and the highest translocation factor (TF) from roots to shoots for Co and Pb for more and less polluted and control sites. *Polygonum arenastrum* has a potential to accumulate Cr even in sites with low chromium concentration in soil. *Polygonum arenastrum* does not show any form of shoot injury at increased levels of F and metals in its tissues. Based on these characteristics we conclude that the ubiquitous *P.arenastrum* may be utilised as a relevant indicator of contamination in industrial zones and may function as an early warning system of increased toxicity in the environment.

1. Introduction

Trace elements are natural components of Earth's crust; however, human activity has dramatically increased the bioavailable fraction of these polluting minerals. Being biologically non-degradable, once discharged to the environment trace elements become an intrinsic part of habitats (Lei et al., 2007). Contamination by these elements may cause persistent damage to biota and must be carefully monitored. In addition to Cd, Cu, Fe, Mn, Ni, Pb and Zn, discharges of fluorine from some industries such as aluminium smelters, coal-fired power plants, phosphate fertiliser plants, glass, brick, tile works, and plastics factories are among the main anthropogenic sources of fluorine pollution (Zhang et al., 2010; Koblar et al., 2011). Nevertheless, monitoring of the highly phytotoxic airborne and particulate fluorine remains rather sporadic (Koblar et al., 2011). Straightaway evaluation of the extent of environmental pollution occurs by surveying the levels of xenobiotics in vegetation especially because of their common occurrence and easy sampling (Čeburnis and Steinnes, 2000; Sardans and Peñuelas, 2005). The use of such bioindicators is an invaluable tool for the evaluation or prognosis of negative consequences of human operations (Markert et al., 2003). Among them, mosses and lichens are one of those most frequently used and the results of many studies suggest their use as biomonitors for various contaminants (Markert et al., 2003; Kłos et al., 2011). Vascular plants are usually not as widespread geographically as bryophytes and do not have such abilities to adapt to various environmental conditions as mosses. However, also higher plants may be used in pollution control (Szczepaniak and Biziak, 2003). *Polygonum arenastrum* Bor. (= *P. aequele* Lindm., *P. aviculare* ssp. *aequale* (Lindman) Ascherson & Graebner), an equal-leaved knotgrass, chosen for this study seems to fulfil requirements for a good ecological indicator. This is a cosmopolitan annual herb of the Eurasian Wide-temperate origin. It is commonly found in open habitats affected by human

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activity (Geber 1989). As part of the *Polygonum aviculare* L. complex (Meerts et al., 1990), these generally weedy species are characterised by low habitat requirements, resistance to harsh environmental conditions, bioindication properties, trace metal accumulation, and suitability for phytoremediation (Costea and Tardiff, 2005; Wei et al., 2009; Mohsenzadeh et al., 2010; Polechońska et al., 2013). However, detailed description of the accumulation abilities of *P.arenastrum*, and especially the distinction between shoots and roots, is not available. Particularly in industrial areas a reliable bioindicator may be very helpful for early detection of increased contamination of the environment with the investigated toxins. In this sense, the paper presents a novelty regarding use and reliability of a new bioindicator, common, widespread and comparable to non-contaminated areas. According to our knowledge there are no publications and there is a shortage of investigations on the bioindication capacity of this species. Additionally, *P.arenastrum* is frequently used for its medicinal purposes (Cong et al., 2012). Natural sites of this plant may be affected by industry both through local or long-range transport, which can lead to the contamination of vegetation for example by metals. Therefore, evaluation of *P.arenastrum* accumulating abilities is necessary also to ensure consumer safety. The aim of this study was to investigate the impact of six various polluting industries on metal and fluorine levels in *P.arenastrum* and whether this species may serve as a relevant bioindicator of contamination in industrial zones. To evaluate this we tested the following hypotheses: 1) concentrations of F and metals in *P.arenastrum* are related to the concentration of the same elements in soil, 2) *P. arenastrum* has the ability to accumulate at least some elements, 3) above-ground parts of *P. arenastrum* should not show injury at F and metal levels in its tissues toxic for other plants.

2. Materials and methods

2.1. Sampling design

In the Lower Silesia, Wielkopolska and Opole Provinces of Poland, six polluting industrial sites were selected (Fig. 1): 1) copper smelter in Legnica, 2) chlor-alkali plant in Brzeg Dolny, 4) former ferrous-chromium smelter and active combustion smelter in Siechnice, 5) power plant in Opole, 6) cement plant in Górażdże and 7) coke plant in Zdzieszowice. A control site (3) relatively free from pollution was selected in the Barycz River Valley Landscape Park near Milicz in an area with similar climate and soil conditions (Pawlak, 1997).

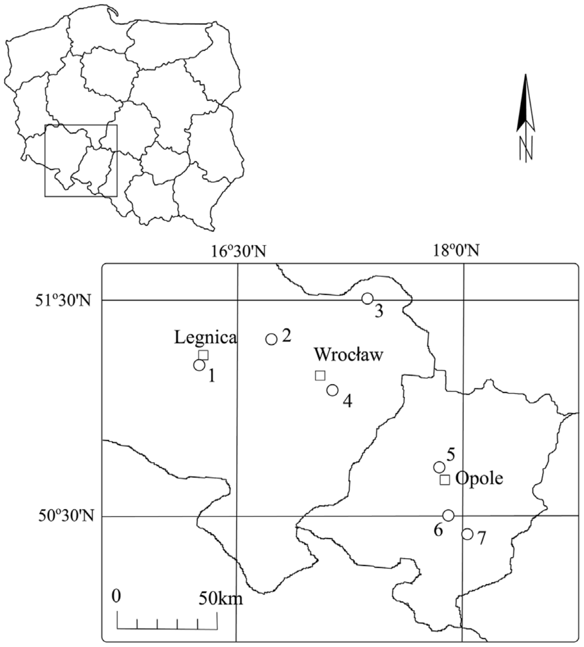

Fig. 1. Map showing the sampling locations.

P.arenastrum samples were collected from the centre of the industrial sites along four transects (S, E, N, and W). The sampling sites were selected at distances starting as close as possible to the factory being the source of pollution (at ~0.75 km), and subsequently further away at 1.5, 3 and 4.5 km in each of the four directions giving altogether 16 examined areas around each polluter. The same number of sampling sites were selected in the control site. The total number of sites affected by six polluting factories was 90. In some sites the species were absent: in Siechnice (N, 1.5 km and W, ~0.75 km); Brzeg Dolny (N, ~0.75 km and E, 1.5 km); Legnica (N and W, ~0.75 km). Selection of distances was according to Franzaring et al. (2006) and Divan Junior et al. (2009) who established such a sphere of fluorine deposition effects from the emission source. At each sampling site 25 m × 25 m squares were selected (Varela et al., 2015) which were further divided into 1 m × 1 m sub-squares, of which 5 were selected randomly. From each of the 5 sub-squares, 30 *P.arenastrum* plants were collected randomly. From each sub-square, soil samples were collected at 0–15 cm which is the depth of root penetration of the species in the examined areas established in preliminary investigation. The collected plants were rinsed in distilled water and divided into roots and shoots. Plants were homogenised in an IKA Labortechnik M20 laboratory mill. Stones, litter, and organic particles were eliminated from the soil samples which were further homogenised in a mortar grinder (Fritsch Pulverisette 2) and sieved through a 2 mm sieve shaker (Morek Multiserw LPzE-2e).

2.2. Soil and plant analysis

Soil pH_{H2O} with distilled water (soil/water ratio 1:2.5) was measured potentiometrically with a HANNA Instruments HI 9107 pH meter with a glass electrode. Before analysis, soil and plant samples were dried at 50 °C until constant weight. Plant-available soil concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were analysed by extraction with 1 M ammonium acetate-EDTA (pH 4.65) for 30 min (5 g dry soil in 50 mL) (Cottenie et al., 1982). Total metal concentrations in soil and in plants were analysed as follows: 300 mg of plant and soil samples (in three replicates) were digested with 3 mL of ultra pure nitric acid (65%) and 2 mL of ultra pure perchloric acid (70%) in a microwave oven (CEM Mars 5). The digests were then diluted with deionised water and analysed for Fe, Mn, and Zn by Flame Atomic Absorption Spectrometry (Avanta PM from GBC) and for Cd, Co, Cr, Cu, Ni and Pb by Graphite Furnace Atomic Absorption Spectrometry (PinAAcle 900Z from Perkin-Elmer): 300 mg of plant and soil samples (in three replicates) was digested with 3 mL of ultra pure nitric acid (65%) and 2 mL of ultra pure perchloric acid (70%) in a microwave oven (CEM Mars 5). The digests were then diluted with deionised water, filtered and analysed for Fe, Mn, and Zn by Flame Atomic Absorption Spectrometry (Avanta PM from GBC) and for Cd, Co, Cr, Cu, Ni and Pb by Graphite Furnace Atomic Absorption Spectrometry (PinAAcle 900Z from Perkin-Elmer). We did not dissolve silicon compounds by adding hydrofluoric acid (HF). All elements were analysed against Atomic Absorption Standard Solution from Sigma Chemical Co. and blanks with the same matrix as the samples and were treated as samples. Results of metal concentrations were calculated on a dry weight basis. The accuracy of the methods was checked against Chestnut Soil, Bainaimao and Bayan Obo, Neil Mongol in China GBW07402 (GSS-2) and Poaceae (mixture) IPE 952WEPAL Certified Reference Materials (ESM 1 and 2). Mercury was assayed using an AMA 254 Advanced Mercury Analyser. F concentration in soil was determined using a method described by Frankenberger et al. (1996) and in plants by the AOAC method (Horwitz, 2000) using a HANNA Instruments HI 9107 device with a combined ion selective fluoride electrode (Sentek).