

Environmental Survey of Heavy Metals in the Yiluo Basin of East-Central China: Water, Soil and Plants

Ryunosuke Kikuchi, Carla S. Ferreira, Antonio D. Ferreira

Abstract— China's economy has grown at an average of 10% over the last 10 years, but the rapid urbanization and industrialization has released large volumes of pollutants. As it is reported that China is facing an environmental crisis, we carried out a field survey in Luoyang city, which is the center of industrial activities in the Yiluo basin, in order to draw a simple picture of the current environment. The obtained results show that sampled water contained Zn and Pb in rich amounts, soil samples contained large amounts of Zn, Pb, Mn, Cu, Cr and Al, and plant samples (e.g. squashes) contained considerable amounts of Al in particular. The measured metal contents exceed not only the European standard but also China's national standard. Chinese farm products are supplied to the European market. In this sense, the issue associated with metal contamination is not local but global (European concern in particular). It is important to establish a natural reference (i.e. background level) in order to properly assess the contamination degree due to human activities, but this subject remains for a future study.

Index Terms— China, Environmental contamination, heavy metals, water, soil, plants.

I. INTRODUCTION

China's environmental crisis is one of the most pressing challenges to emerge from the country's rapid industrialization. Its economic rise, during which the value of gross domestic product (GDP) grew on average 10% each year for more than a decade, has come at the expense of its environment and public health [1 & 2]: (i) China is the world's largest source of carbon emissions, (ii) the air quality of many cities fails to meet international health standards, and (iii) severe contamination of water has compounded land deterioration. Environmental degradation threatens to undermine the country's growth and exhausts public patience with the pace of reform. It has also bruised China's international standing and endangered domestic stability as the ruling party faces increasing scrutiny and public discontent.

China's economy has shown uneven regional growth. Economic growth has been more rapid in the coastal regions of eastern China than in the other regions since the Chinese economic reform in 1978 [3]. Several factors are likely to have caused the differences in regional development [3]; for

example, the regional disparity may be due to different paces of development of private firms, different regions have experienced different changes in industrial structure, etc.

The rapid urbanization and industrialization require enormous amounts of fresh water and release large volumes of wastewater. To make up for the shortage of water, sewage irrigation has been widely used in China since 1972 as an important supplement and alternative water resource [4]. The benefits of sewage water irrigation are that it not only reduces freshwater demand but also adds a certain amount of nutrients and organic matter into the soil [5]. However, wastewater may contain heavy metals such as Cu, Pb, Zn, Cd, Ni, Cr, Mn, and Hg [6 & 7]. As a result of long term sewage irrigation and industrial air pollution, heavy metal accumulation in agricultural ecosystems is almost inevitable [8] and it has been recorded in south-eastern China [9]. This accumulation may cause potential risks to human health via the food chain such as soil-plant-(animal)-human and the intake of contaminated water [10]. As sewage irrigation has been using untreated sewage and reclaimed wastewater over the long term, soil quality has become a critical issue [11].

Most terrestrial life needs a continual source of water for sustenance, and soil is an essential medium for plant growth in most terrestrial ecosystems, providing nutrients, water, physical support, and biological interactions with roots [12]; that is, soil, water and crop growth are closely linked in nature. Focusing attention on this link, we carried out an environmental survey in the Yiluo basin in order to draw a simple picture of the current metal contamination in China.

II. SURVEY FIELD

The Yiluo basin is located in the east-central region of China; i.e. this basin is situated about 650 km to the south-southwest of Beijing and about 1,000 km to the west-northwest of Shanghai [13]. The area encompasses about 2,530 km² [13]. Luoyang is the largest city in the Yiluo basin, with a population of about 2 million. Agriculture (wheat and maize) and manufacturing (glass and farm machines) are the basin's main industries [13 & 14].

The geographical setting of the region is also significant because the Yiluo River and its tributaries occupy a vast fertile basin surrounded by the Huanghe River to the north and by mountain ranges on the other three sides. The advantages of this combination of protective isolation and access along the valleys to other regions are reflected in the role the basin has played in Chinese history, no less than nine dynasties having established their capitals there [14].

This region has a temperate, sub-humid monsoon climate, with annual average precipitation of about 635 mm and the

Ryunosuke Kikuchi, CERNAS, ESAC - Politécnico de Coimbra, Coimbra, Portugal,

Carla S. Ferreira, CERNAS, ESAC - Politécnico de Coimbra, Coimbra, Portugal,

Antonio D. Ferreira, CERNAS, ESAC - Politécnico de Coimbra, Coimbra, Portugal,

heaviest rainfall in July. The summers are warm (July average of 27.8°C) and the winters cool (January average of -0.3°C). Topographically the area is characterized by high plateaux of loess (wind-blown silt), most of which was deposited during cold dry climatic episodes that occurred in the Pleistocene period (ca. the past two million years) [14].

III. MATERIALS AND METHODS

As stated in the introduction, the main purpose is to draw a simple picture of the current situation in China. In view of this purpose, a survey was performed in Luoyang city, which is the center of industrial activities in the Yiluo basin (figure 1A). Each sampling (n = 2) point is shown in figure 1B. Attention was mainly focused on metal elements due to concern over metal contamination over the long term (refer to the introduction).

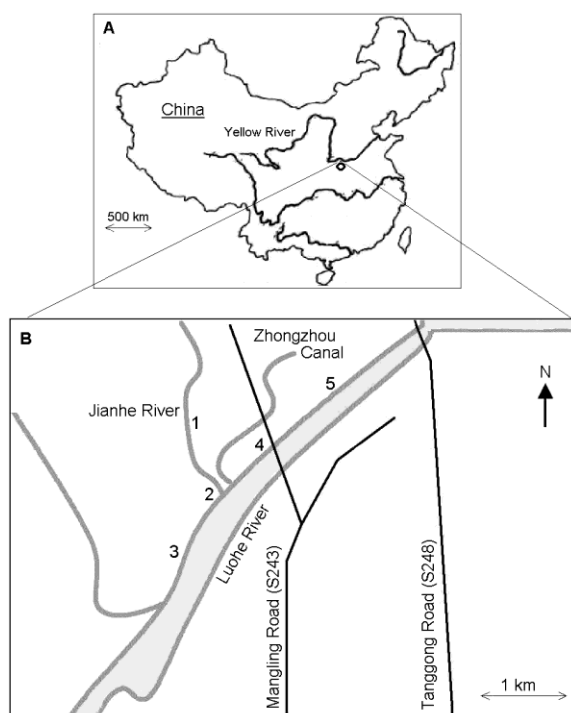


Figure 1. Location of the survey field (the Yiluo basin): A – map showing Luoyang in China, and B – numbers showing the sample points in Luoyang.

Each sampling point (figure 1B) and local plant are briefly characterized in table 1 – the same type of plant could not be located at each sampling point, so there was nothing for it but to take a different local plant at each sampling point.

Table 1. Location properties and types (common names and Latin names) of plant sampled in each point shown in figure 1B

Point No.	Location property	Plant type
1	Acrid odor in the surroundings	<i>Cucurbita maxima</i> (Violales, Cucurbitaceae)
2	Marshy and muddy	No sampling
3	Rich terrestrial biodiversity	<i>Cirsium setosum</i> (Campanulales, Asteraceae)
4	Barren soil and waste deposition	<i>Plantago depressa Willd</i> (Plantaginales, Plantaginaceae)
5	Muddy and oil-like in the river	<i>Cirsium setosum</i> (Campanulales, Asteraceae)

A. Sampling

Soil samples (ca. 20 g) were taken at each point at a depth of 0–20 cm, and water samples (ca. 100 ml) were taken from the surface of the river near each point. Plant samples (a few grams) were also taken at each point. The soil samples and the plant samples were stored in plastic bags, and the water samples were stored in high-density polyethylene bottles. After all the samples were transported to a laboratory, they were preserved in a cold dark place until the start of the chemical analysis.

B. Pre-treatment

Plant samples were dried at room temperature (ca. 20°C), and soil samples were dried at 110°C for 11 hours. After drying, the soil samples were put through a sieve with a 2-mm grid, and the plant samples were cut into fine pieces. After this pre-treatment, metal elements were extracted from the pre-treated samples by means of 1N sulfuric acid and 1N nitric acid. Extraneous materials were separated from the extract liquids with a filter paper (No. 5B) and a centrifuge (3000 rpm, 5 minutes). The water samples were poured through a funnel with a filter paper inserted (No. 5B) in order to separate insoluble particles.

C. Metal determination

Attention was mainly focused on metal elements, so the following metals contained in the plant samples, the soil samples and the water samples were determined by inductively coupled plasma emission spectrometry (Perkin Elmer, Optima 5300DV): Zn, Pb, Se, Mn, Cu, Cr, Cd, As, and Al. These metal contents were calculated from spectra which had a standard error of less than 10% based on a calibration curve. The results obtained from the metal analyses are expressed as concentration.

IV. RESULTS

All data are shown as the average values, which are considered to be representative. As it was impossible to collect plant and soil samples at sampling point No.2, which was a marshy area, there are no data on the plant and soil.

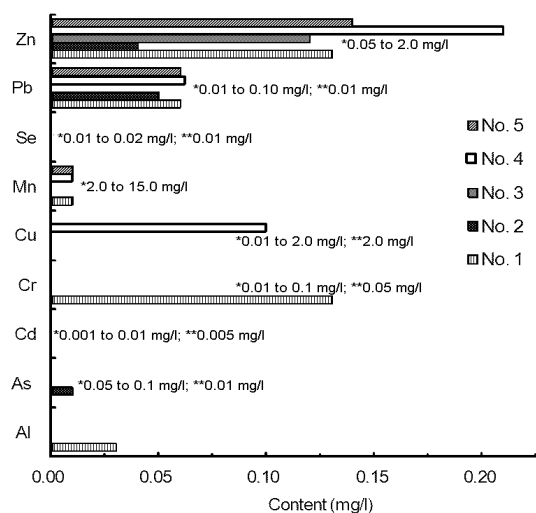


Figure 2. Metal contents of water at sample points numbered in figure 1B. *Chinese guidelines for indicating water category I (high quality) to V (poor quality) and **EU guidelines for drinking water (reviewed in [18])

A. Metals contained in the water samples

The summary of results (figure 2) shows that the Zn content was high and the Pb content was comparatively high at all points. The Cu content and the Cr content were also high at sample point No. 4 and No. 1 respectively. The Pd contents in all the samples did not accomplish the limit value based on European guidelines for drinking water. The Cr content at sample point No. 1 considerably exceeded the limit value recommended by European guidelines.

B. Metals contained in the soil samples

It follows from figure 3 that the sampled soils contained various metals. As figure 3 uses a log-10 scale for the X axis, each increment along the X axis represents an increase by a factor of 10 rather than equal increments; to put it differently, the metal contents vary quite widely depending on the sample point. Furthermore, it should be noted that the Al content was quite high at every sample point. The values obtained at all the sampling points exceeded the permissible Cd level established by Chinese guidelines for soil quality.

The contents of Zn, Pb and Cu also surpassed the Chinese guideline levels at several sampling point. The Se content collected at sampling point No. 2 was greater than the German limit value. The contents of Cu and Cr also exceeded the Switzerland guideline and the Netherlands guidelines at two sampling points. These European guidelines are just referred as referential comparison.

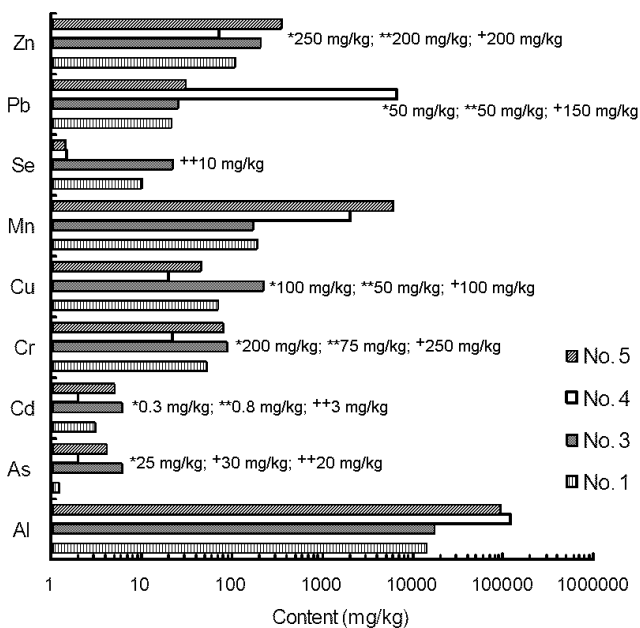


Figure 3. Metal contents of soil at sample points numbered in figure 1B. *Chinese guidelines for soil (reviewed in [19]), **Switzerland guidelines, +Netherlands caution values and ++German limit values (reviewed in [18])

C. Metals contained in the plants

There is a tendency for the pattern of metals in the plant samples (figure 4) to differ from that in the water samples and the soil samples. Although the sampled plants contained some degree of all the metals, only the Al content was high in all the samples except for the sample collected at point No. 4. *Cucurbita maxima* at point No. 1 (table 1) contained the most aluminum. This plant is a specie of cultivated squash, and it is one of the most diverse domesticated species [20].

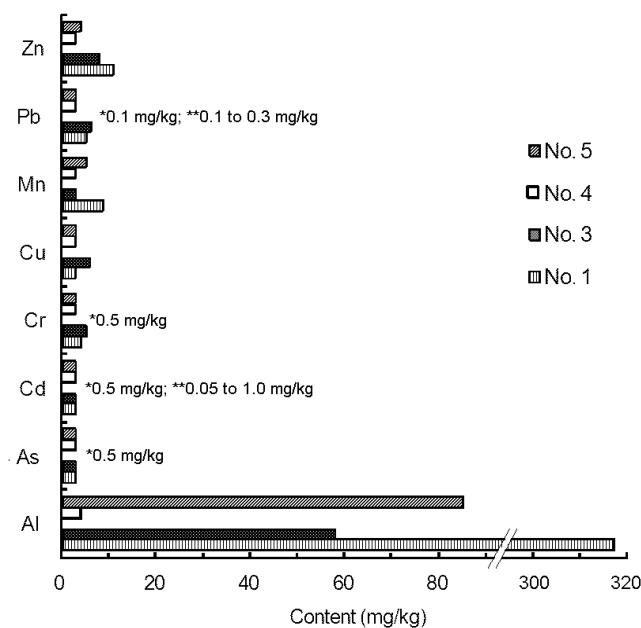


Figure 4. Metal contents of plants at sample points numbered in figure 1B. *Chinese food guideline [20] and **European Union guidelines for different cereals and horticulture products [22]

V. CONSIDERATION

As seen in figures 1, 2 and 3, most water, soil and plant samples contained various metals: the water samples contained Zn and Pb in rich amounts; the contents of Zn, Pb, Mn, Cu, Cr and Al were high in the soil samples; and the plant samples contained a high amount of Al in particular. It should be noted that at least one of metal elements exceeded the guideline level at all the sampling points.

A. Measured values and regulation values

Definition of the regulation value is not a simple issue in practice. Different nations have adopted different, more or less arbitrarily defined levels – each reflecting their own local circumstances [23]; for example, only a few member states of the European Union (EU) currently have specific legislation on soil protection, and soil is not subject to a comprehensive and coherent set of rules in the Union [24]. Existing EU policies in areas such as agriculture, water, waste, chemicals, and prevention of industrial pollution do indirectly contribute to the protection of soils. But as these policies have other aims and scopes of action, they are not sufficient to ensure an adequate level of protection for all soils in Europe [24]. A referential comparison of the measured values with representative European standards (Germany, Switzerland and Netherland reviewed in [25]) shows that all the metal contents in the soil exceed the European guideline levels except for the Al content. A referential comparison of the metal contents in the plant samples with Chinese food guidelines [21] shows that some metal contents in the squash (*Cucurbita maxima* at sample point No. 1) clearly exceed the standard levels of 0.05 mg/kg Cd or below, 0.1 mg/kg Pb or below, and 0.5 mg/kg Cr or below.

B. Natural sources and human sources

Although high metal contents were determined in the samples, it cannot be asserted that the researched field (i.e. Luoyang in the Yiluo basin) has been contaminated with

metals as a result of human activities. The sources of heavy metals can be classified into five categories [26]: (i) geologic weathering, (ii) industrial processes of ores, (iii) the use of metals and metal components, (iv) leaching of metals from garbage and solid waste dumps, and (v) animal and human excretions. That is, the input of heavy metals to the environment can be basically divided into natural sources (e.g. weathering) and human sources. It is important to establish a natural reference (i.e. background level) in order to qualify the contamination degree and compare the specific metals that have different concentrations (reviewed in [27]). Figure 5 illustrates the schematic distribution of metal contents in the environment. It remains for a future study to measure background levels of metals in order to estimate real contamination due to human activities.

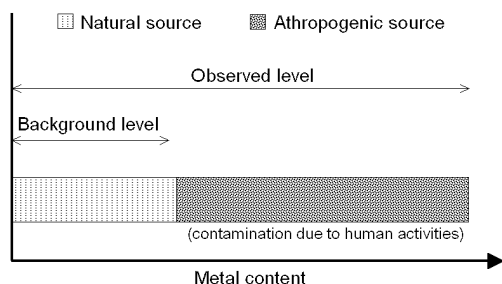


Figure 5. Schematic drawing of different sources and observed level of metal

C. Potential risk of high Al content in plants

The term "heavy metal" has been used extensively in the past to describe metals that are environmental pollutants. There are some metals that are not heavy – for example, aluminum (Al), which has a relative density of only 1.5 [28]. Although it is proposed that the Al toxicity is low or null [29], this metal is an extremely important pollutant [30]; the gills of fish are particularly susceptible to Al poisoning, and this Al has also been implicated in Alzheimer's disease in humans and may be deposited in the brain [30].

As seen in figure 4, a high Al content was found in the squash (*Cucurbita maxima*). Nearly 25 million tons of pumpkins and squash were produced around the world in 2013, and growth was particularly strong during the 1990s until the mid-2000s, largely due to the double-digit rise in Chinese production [31]. China actually consumes most of this production. On the other hand, Spain is the largest exporter of pumpkins and squash. Spain grows these products on about 11,000 hectares of land, about 3% of the area used in China [31]. But productivity is much higher, resulting in production equal to about 8% that of China. Spain mostly supplies these agricultural products to other European markets [31]. In this sense, it can be said that the food risk associated with farm products containing Al is not local but global. Aluminum makes up a significant portion of the earth's crust, and soil and water contain aluminum [28]. It is therefore considered that most foods contain at least trace amounts of aluminum. Ingesting small amounts of aluminum may not cause harm; however, there is a possibility that the long-term intake of a large amount of Al may be potentially toxic to humans and the ingested Al may build up within the brain. Studies have not yet conclusively proven a connection.

Bauxite is a naturally occurring ore from which alumina

and aluminum are produced [28]. Australia is the top producer of bauxite, with almost one-third of the world's production, followed by China [32]; that is, natural Al resources are abundant in China, and there are also bauxite deposits in the Yiluo basin. It is hence possible to consider that local plants absorb and accumulate aluminum emitted from natural sources. As stated in the previous section, it is important to distinguish between naturally occurring metal and human-induced metal.

VI. CONCLUDING REMARKS

The presented survey aimed at drawing a simple picture of the current environment in China. In view of the amount of metal contents, it seems that the environment is severely polluted in the Yiluo basin; however, this problem is not local but global because farm products made in China are consumed worldwide. It is not enough to measure pollutants at several points. Distinguishing between natural and anthropogenic metal inputs is left as a future study for enabling a proper environmental strategy to be taken in terms of minimizing metal pollution.

ACKNOWLEDGMENT

The authors are grateful to Mr. L. Tao of Ryukoku University for sampling, laboratorial work and Chinese translation, and to Ms. C. Lentfer for English review.

REFERENCES

- [1] E. Albert, (2016). China's Environment Crisis, in CFR Backgrounder. New York: Council on Foreign Relations, press release on 18 January.
- [2] The Economist Newspaper Ltd., "All dried up", in *The Economist*. London: The Economist Newspaper, press release on 12 October 2013.
- [3] S. Lee, D.W. Oh, (2015). Economic growth and the environment in China: Empirical evidence using prefecture level data. *China Economic Review* 36, 73-85.
- [4] H. Yang, K.C. Abbaspour, (2007). Analysis of wastewater reuse potential in Beijing. *Desalination*, 212, 238-250.
- [5] J. Horswell, T.W. Speir, A.P. Schaik, (2003). Bio-indicators to assess impacts of heavy metals in the land-applied sewage sludge. *Soil Biology & Biochemistry*, 35, 1501-1505
- [6] G.J. Wilbers, M. Becker, L.T. Nga, Z. Sebesvari, F.G. Renaud, (2014). Spatial and temporal variability of surface water pollution in the Mekong Delta, Vietnam. *Science of the Total Environment* 485-486, 653-65.
- [7] X. Yuan, T. Li, J. Li, H. Ye, M. Ge, (2013). Origin and Risk Assessment of Potentially Harmful Elements in River Sediments of Urban, Suburban, and Rural Areas. *Polish Journal of Environmental Studies* 22(2), 599-610.
- [8] J. Yang, Z.C. Huang, T.B. Chen, M. Lei, Y.M. Zheng, G.D. Song, Y.Q. Liu, C.S. Zhang, (2008). Predicting the probability distribution of Pb-increased lands in sewage-irrigated region: a case study in Beijing, China. *Geoderma* 147, 192-196.
- [9] S. Yu, Q. Wu, Q. Li, J. Gao, Q. Lin, Q. Xu, S. Wu, (2014). Anthropogenic land uses elevate metal levels in streamwater in an urbanizing watershed. *Science of the Total Environment* 488-489, 61-69.
- [10] R. Wuana, F.E. Okieimen, (2011). Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. *ISRN Ecology* 2011, 1-20.
- [11] Ministry of Environmental Protection of China, (2014). *National soil pollution investigation government bulletins* [Online]. Available: http://www.mlr.gov.cn/xwdt/jrxw/201404/t20140417_1312998.
- [12] Food Alliance, (2016). *Soil & water conservation* [Online]. Available: <http://foodalliance.org/about/faqs>
- [13] R. Zhao, (2009). Flow net analysis of groundwater in Yiluo River Basin. *Bulletin of Geo-environmental Science* 11, 81-87.
- [14] A. Rosen, (2001). Environmental and cultural change in Yiluo basin, east-central China. *Archaeology International* 5, 51-53.

- [15] National Meteorological Center of the China, Meteorological Administration, (2016). *Government bulletin from Luoyang city* [Online]. Available: http://eng.weather.gov.cn/forecast_city.php?sc=57073
- [16] LEAM - Licenciatura em Engenharia do Ambiente, (2005). Practical class protocol - solid waste treatment. Escola Superior Agrária, Coimbra (in Portuguese).
- [17] General Bureau of China National Environmental Protection and General Administration of Quality Supervision, Inspection and Quarantine of the People's republic of China (2002). Environmental Quality Standards for Surface Water GB 3838-2002. *General Bureau of China National Environmental Protection and General Administration of Quality Supervision, Inspection and Quarantine of the People's republic of China*, Beijing, China (in Chinese).
- [18] R. Kikuchi, T. Gorbacheva, (2008). Focus on understanding the relation between lakes and pollution – model-based approach and case study of subarctic lake. In: *Lake Pollution Research*, F.R. Miranda and L.M. Bernard (eds), Nova Science Publishers, Hauppauge (NY), pp. 107-131.
- [19] L. Tao, (2015). Environmental Survey in the Yulio basin near Yellow River. BSc. Thesis in Ryukoku University, Otsu (in Japanese).
- [20] M. Ferriol, B. Pico, F. Nuez, (2004). Morphological and Molecular Diversity of a Collection of Cucurbita maxima Landraces. *Journal for the American Society for Horticultural Science* 129 (1). 60-69.
- [21] Standardization Administration of China, (2012). National Food Standard, No. GB2762-2012, Beijing (in Chinese).
- [22] Commission Regulation (EC) No 1881/2006, (2006). Setting maximum levels for certain contaminants in foodstuffs. *The Commission of the European Communities* [Online]. Available: <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02006R1881-20140901&from=PT>.
- [23] B.J. Alloway, (1995). *Heavy Metals in Soils*, 2nd edition. London: Blackie Academic & Professional.
- [24] Directorate-General for Environment, (2016). *Soil*, [Online]. Available: http://ec.europa.eu/environment/soil/index_en.htm
- [25] M.J. Haigh, (1996). Soil contamination and land reclamation – notes from the coal fields of Europe. *Envis Newsletter* 1 (3), 1-10.
- [26] U. Forstner, G.T.W. Wittman, (1979). *Metal pollution in the aquatic environment*. Berlin: Springer.
- [27] R. Kikuchi, T. Gorbacheva, (2008). Focus on understanding the relation between lakes and pollution – model-based approach and case study of subarctic lake, in *Lake Pollution Research*, F.R. Miranda and L.M. Bernard, Eds, New York: Nova Science, pp. 107-131.
- [28] J. Daintith (ed), (1995). *A Concise Dictionary of Chemistry*. Oxford: Oxford University Press.
- [29] J.M. Wood, (1974). Biological cycles for toxic elements in the environment. *Science* 183, 1049-1052.
- [30] C.H. Wall, S.P. Hopkin, R.M. Sibly, D.B. Peakall, (2001). *Principles of Ecotoxicology*. New York: Taylor & Francis.
- [31] V. Romei, (2015). China produces the most pumpkins, in the Financial Times. London: The Financial Times Ltd., press release on 31 October.
- [32] P.A. Plunkert, (1998). *Primary Aluminum Plants Worldwide – 1998*. Reston: U.S. Geological Survey.

Ryunosuke Kikuchi was awarded a PhD from Sofia Technical University for his studies of the recycling of air pollutants. He was a project coordinator at the Ministry of the Environment in Bulgaria and a researcher at University of Helsinki in Finland. He has been a researcher of CERNAS in Portugal since 2002 and a professor of Ryukoku University in Japan since 2010. His present research focuses on the combination of environmental technology and strategy with social benefits.

Carla S. Ferreira was awarded a PhD from Aveiro University for her studies of peri-urban areas. She has been involved in several Portuguese and European research projects, and performed researches at Swansea University in the UK and at Cornell University in the USA. She is currently a researcher of CERNAS in Portugal. Her present research is connected with the impact of land-use changes on soil and water degradation.

Antonio D. Ferreira was awarded the prize for best PhD in Global Change held in Portugal from 1995 to 2000. He coordinated a Life Environmental Project that was considered by the European Commission as one of the Best Life Environmental Projects in 2007-2008. He is a coordinator of CERNAS and professor at ESCA - Polytechnic Institute of Coimbra in Portugal. He has broad experience of research in Africa and South America.