Phytoextraction and management options to reduce cadmium and arsenic in food crops

Fang-Jie Zhao and Steve P. McGrath

Rothamsted Research, Harpenden, Hertfordshire AL5 2JQ, UK
Fangjie.Zhao@bbsrc.ac.uk

Abstract: Cadmium and arsenic are two toxic elements that may accumulate in food crops to levels unsafe for human consumption. Here we present case studies on the potential of phytoextraction and management options to reduce Cd and As accumulation in food crops. Small-scale field trials showed that four croppings of the Cd hyperaccumulator *Thlaspi caerulescens* removed 14 – 47% of soil Cd. In a series of long-term sewage sludge trials, Cd concentration in wheat grain can be predicted reliably from soil total Cd, pH and organic matter content; from this relationship it is possible to predict with reasonable confidence the soil conditions that will not lead to the exceedance of wheat grain Cd over the current EU maximum permissible concentration. Recent studies have shown that paddy rice is particularly efficient at As accumulation due to two reasons: 1) reductive mobilization of arsenic under the anaerobic conditions of the submerged paddy soil; and 2) inadvertent uptake of arsenite through the highly efficient pathway of Si uptake in rice. A number of management options may be used to reduce As accumulation in rice, including periodic draining of paddy water, Si fertilization, and selection and breeding of low As cultivars of rice.

Keywords: Arsenic, cadmium, rice, wheat, soil contamination, phytoextraction.

1. Introduction

Arsenic (As) and cadmium (Cd) are non-essential toxic elements that may accumulate in food crops to levels posing potential risks to human health. There are national or international maximum permissible limits on these elements in food crops; exceedance of these limits will affect their sale and use. Transfer of toxic elements may be further exacerbated by soil contamination or by specific soil conditions leading to enhanced bioavailability. In this paper, we examine the potential of phytoextraction and management options to reduce Cd and As accumulation in food crops.

The efficiency of phytoextraction depends on the level of contamination in soil and the amount of metals/metalloids accumulated by plants. The metal removal rate can be estimated using plant biomass production and the bioconcentration factor (i.e. the ratio of metal concentration in plant shoots to that in soil) (*1*) (Figure 1). Assuming a biomass production of 10 tonnes per hectare (t ha^{-1}) per crop, which is easily attainable for many agricultural crops, the bioconcentration factor would need to be 20 or greater to decrease the soil metal concentrations by 50% in fewer than 10 crops. With a high biomass of 20 t ha^{-1} per crop, a bioconcentration factor of greater than 10 is required. Figure 1 shows that phytoextraction is unlikely to be feasible if the bioconcentration factor is <10; this applies to most plant species as they have limited capacities for metal uptake or, more importantly, root to shoot translocation. Some hyperaccumulators have very high bioconcentration factors (10 – 100) when grown in contaminated soils, e.g. an ecotype of *Thlaspi caerulescens* from southern France (*2*) and the As hyperaccumulator *Pteris vittata* (*3*). Recently, Murakami *et al.* (*4*) reported high bioconcentration factors (10 – 44) for Cd in several Indica rice cultivars when grown under aerobic soil conditions, and demonstrated their abilities for phytoextraction of Cd.

2. Phytoextraction of Cd with *Thlaspi caerulescens*

We have tested the phytoextraction potential of *T. caerulescens* (the Ganges ecotype from southern France) in a field experiment previously contaminated with different levels of Cd (0.4 – 9.8 mg kg^{-1}) due to past additions of sewage sludge (*5*). The biomass production was generally small (<1 t ha^{-1} dry weight) with this plant; however, in one season when the plants were allowed to over-winter and grow for 14 months, higher biomass yields (0.7 – 3.7 t ha^{-1}) were obtained. The bioconcentration factor for Cd was high in all years (31 – 92), thus compensating for the relatively low biomass yield of this plant species. Over the four harvests made between 2000 – 2004, *T. caerulescens* removed 14 – 47% of the Cd in the top soil (Fig. 2). Furthermore, there was a very good agreement between the measured concentrations of Cd in the soils after phytoextraction and those calculated from plant uptake assuming a uptake zone of 20 cm (Fig. 3), indicating that the uptake of Cd by *T. caerulescens* was indeed mainly from the top 20 cm soil.

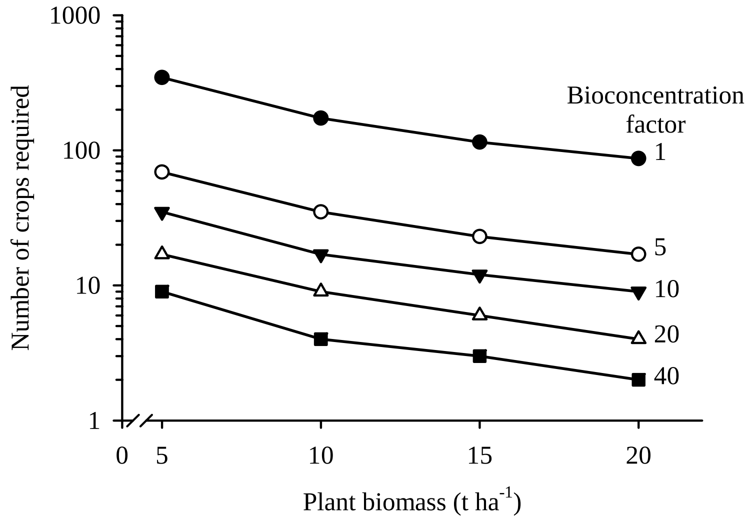

Fig. 1. Model calculations of the number of crops (harvests) required to halve metal concentrations in the top soil, assuming that the metal taken up by plants is from the top 20 cm of soil (McGrath & Zhao, 2003).

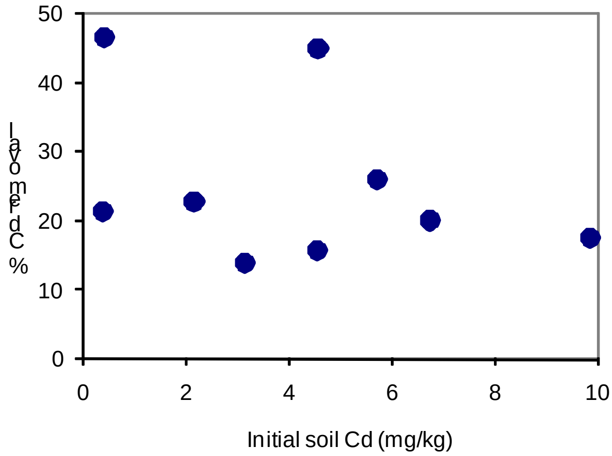

Fig. 2. % removal of Cd from soil by four harvests of *Thlaspi caerulescens* (Ganges).

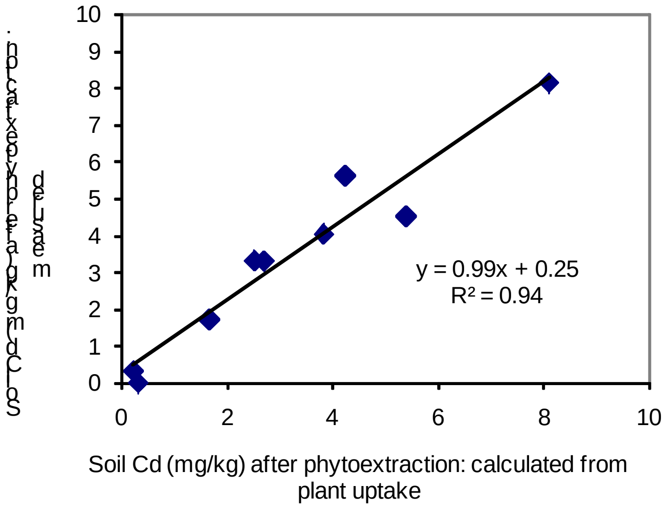

Fig. 3. Soil Cd concentrations after phytoextraction: agreement between measured and calculated values.

3. Management options to reduce Cd accumulation in crops

While phytoextraction may be feasible for moderately contaminated soils, it has not been used on agricultural soils on a large scale in the UK due to the cost and the lengthy duration required. Soil management options that can be used to limit the accumulation of Cd to food crops are likely to be more practical. In a series of field trials (9 sites across the UK) assessing the effects and risks of sewage sludge on soil and crops, it was found that the concentration of Cd in wheat grain can be predicted quite reliably from soil total Cd, pH and organic matter content according to the following regression equation(*6*) (Fig. 4):

$\log_{10}$ (Grain Cd) = 3.9 + 0:86 $\log_{10}$ (Soil total Cd) – 0.25 pH - 0.75 $\log_{10}$ (Soil organic carbon)

n = 1408, $R^2_{adj.}$ = 0.78

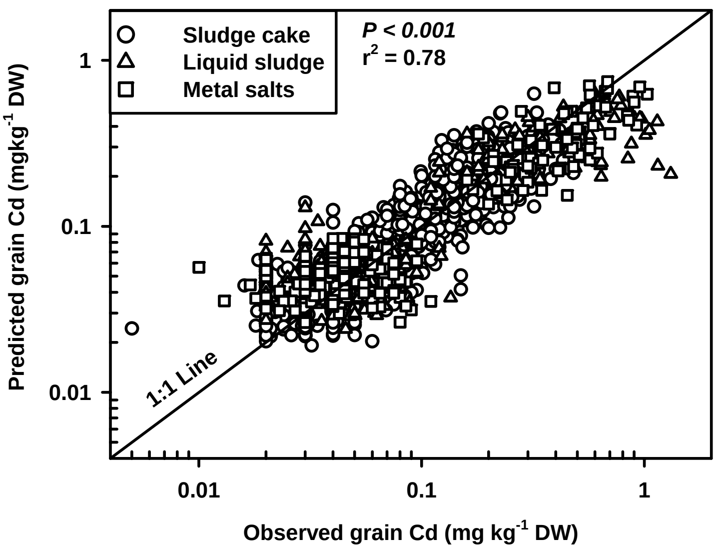

Fig. 4. The relationship between measured and predicted Cd concentrations in wheat grain from 12 field experiments in three growing seasons (*6*).

From the above equation, it is possible to predict with reasonable confidence the soil conditions that will not lead to the exceedance of wheat grain Cd over the current EU maximum permissible concentration (MPC) of 0.2 mg kg^{-1} fresh weight (= 0.235 mg kg^{-1} dry weight) (Fig. 5). This information can now be used by farmers and companies who apply sewage sludge to land because these two soil factors (soil pH and Cd concentration) can be controlled in practice.

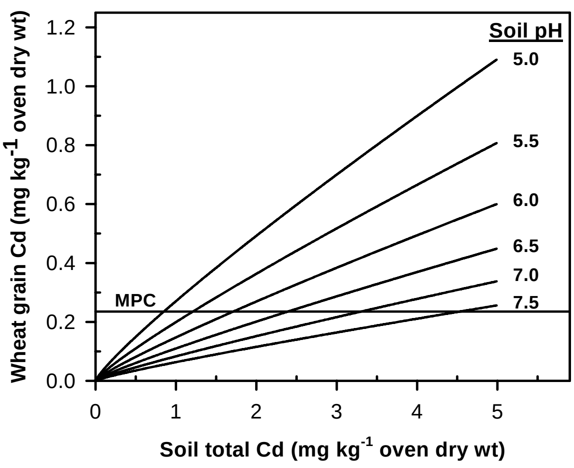

Fig. 5. Predicted upper 95% confidence limit for grain Cd as influenced by soil total Cd and pH with organic C fixed at 2.2% (*6*). MPC, maximum permissible concentration in wheat grain.

4. Arsenic accumulation in rice and potential mitigation options

It has been recognized in recent years that consumption of rice can contribute significantly to the intake of inorganic As (As_i) by humans (*7-9*). For populations based on a rice diet and not exposed to high levels of As in drinking water, intake of As_i from eating rice is the dominant source (*9,10*). Even for populations exposed to elevated As_i in drinking water, such as As-affected areas in south Asia, As_i intake from rice is significant, accounting for ~50% (*11,12*). Rice is efficient at As accumulation due to two reasons: 1) enhanced As bioavailability under the anaerobic conditions of submerged paddy soils as a result of reductive mobilization of arsenite (*13-15*); and 2) the inadvertent uptake and transport of arsenite through the Si pathway which is highly efficient in rice (*16,17*).

Several management options may be used to mitigate the problem of excessive As accumulation in paddy rice. Because soil redox potentially controls As mobility in paddy soil, water management can be used to minimize As uptake and transfer into rice grain. In greenhouse experiments, we found that growing rice under aerobic soil conditions for the whole or part of the rice growing season markedly reduces As accumulation in the grain (*15,18*) (Fig. 6). This effect was consistent with the observation that flooding soil induces a rapid mobilization of arsenite into soil solution (*15,18*) . However, one potentially negative effect of aerobic cultivation is the enhanced Cd accumulation.

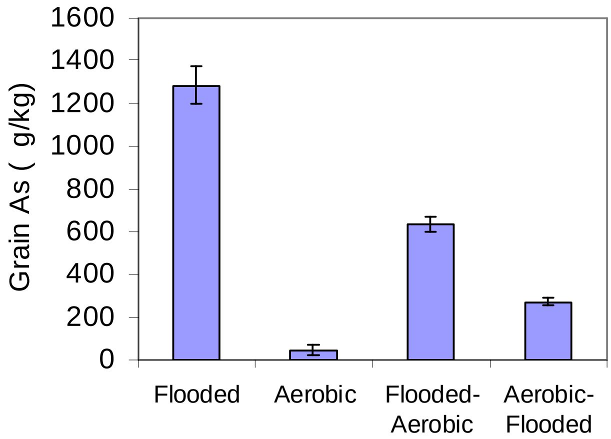

Fig. 6. Effect of watering regime on As accumulation in rice in a greenhouse experiment (*18*). Soil total As = 11.6 mg kg^{-1}. “Flooded – Aerobic” and “Aerobic – Flooded” were treatments in which watering regime was switched at flowering.

Because of the shared uptake pathway between Si and arsenite in rice, it is possible to use Si fertilizer to decrease As accumulation. In a pot experiment, we found that Si fertilization decreased the total As concentration in straw and grain by 78 and 16%, respectively, even though Si addition increased As concentration in the soil solution (*18*) (Fig. 7). Silicon also significantly influenced As speciation in rice grain by enhancing methylation. Silicon decreased the inorganic As concentration in grain by 59% while increasing the concentration of dimethylarsinic acid (DMA) by 33% (Fig. 7).

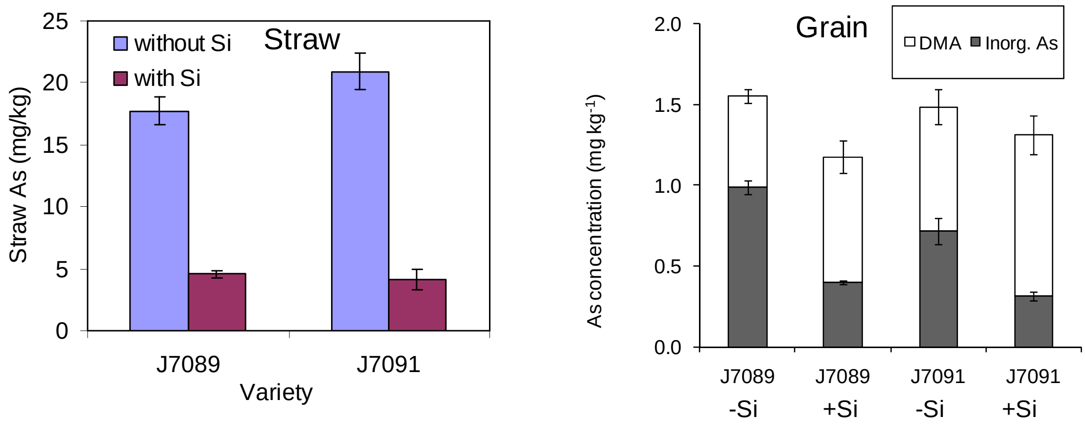

Fig. 7. Effect of Si fertilization on As concentration in straw and As speciation in grain of two Japonica rice cultivars in a pot experiment (*18*).

For poor farmers in Southeast Asia, selection and breeding of low As cultivars may be a more practical option. In field trials at two As contaminated sites in Bangladesh, there were large variations in the concentration of As in grain among the 72 cultivars tested (*19*) (Fig. 8). Cultivars with red bran turned out to contain high concentrations of As. There was a highly significant correlation in grain As concentration between the two field sites, indicating that the genotypic difference was reasonably stable across these two sites.

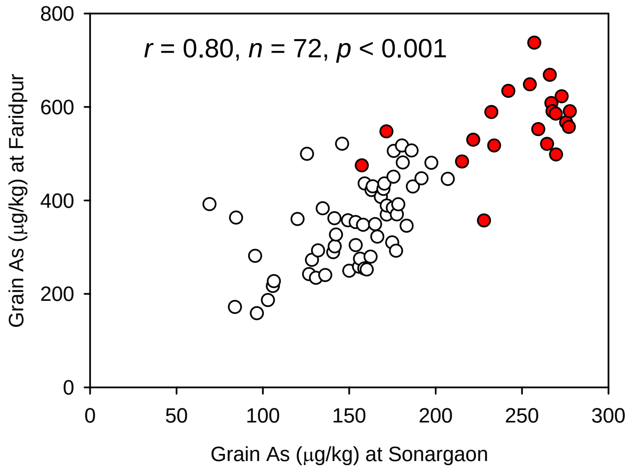

Fig. 8. Correlation in grain As concentration of 72 rice cultivars between two field trials in Bangladesh (*19*). Red symbols indicate cultivars with red bran.

It has not been tested if phytoextraction is a feasible strategy for As contaminated paddy soils. A number of As hyperaccumulating ferns have been identified (*20*,*21*). When grown in As contaminated sites, *Pteris vittata* achieved high bioconcentration factors for As (>20), but a low biomass production (~1 t ha^{-1}) (*22*,*23*). Therefore, biomass production was the limiting factor in these phytoextraction trials. It should also be noted that the hyperaccumulating ferns could be invasive plant species and their introduction to non-indigenous areas should be evaluated carefully with regard to potential ecological consequences.

Acknowledgements

We thank Professor Jian Feng Ma, Professor Andy Meharg, Dr Graeme Norton, Dr Adam Price and Professor Rafique Islam for collaboration. Our research on arsenic was funded partly by a DFID-BBSRC grant (BB/F004087/1). Rothamsted Research is an institute of the UK Biotechnology and Biological Sciences Research Council.

References

(1) McGrath, S. P.; Zhao, F. J. Phytoextraction of metals and metalloids from contaminated soils. *Current Opinion in Biotechnology* **2003**, *14*, 277-282.

(2) Zhao, F. J.; Lombi, E.; McGrath, S. P. Assessing the potential for zinc and cadmium phytoremediation with the hyperaccumulator *Thlaspi caerulescens*. *Plant Soil* **2003**, *249*, 37-43.

(3) Ma, L. Q.; Komar, K. M.; Tu, C.; Zhang, W. H.; Cai, Y.; Kennelley, E. D. A fern that hyperaccumulates arsenic - A hardy, versatile, fast-growing plant helps to remove arsenic from contaminated soils. *Nature* **2001**, *409*, 579-579.

(4) Murakami, M.; Nakagawa, N.; Ae, N.; Ito, N.; Arao, T. Phytoextraction by rice capable of accumulating Cd at high levels: reduction of Cd content of rice grain. *Environmental Science & Technology* **2009**, *43*, 5878–5883.

(5) McGrath, S. P.; Lombi, E.; Gray, C. W.; Caille, N.; Dunham, S. J.; Zhao, F. J. Field evaluation of Cd and Zn phytoextraction potential by the hyperaccumulators *Thlaspi caerulescens* and *Arabidopsis halleri*. *Environ. Pollut.* **2006**, *141*, 115-125.

(6) Chaudri, A.; McGrath, S.; Gibbs, P.; Chambers, B.; Carlton-Smith, C.; Godley, A.; Bacon, J.; Campbell, C.; Aitken, M. Cadmium availability to wheat grain in soils treated with sewage sludge or metal salts. *Chemosphere* **2007**, *66*, 1415-1423.

(7) Schoof, R. A.; Yost, L. J.; Eickhoff, J.; Crecelius, E. A.; Cragin, D. W.; Meacher, D. M.; Menzel, D. B. A market basket survey of inorganic arsenic in food. *Food Chem. Toxicol.* **1999**, *37*, 839-846.

(8) Williams, P. N.; Price, A. H.; Raab, A.; Hossain, S. A.; Feldmann, J.; Meharg, A. A. Variation in arsenic speciation and concentration in paddy rice related to dietary exposure. *Environ. Sci. Technol.* **2005**, *39*, 5531-5540.

(9) Meharg, A. A.; Williams, P. N.; Adomako, E.; Lawgali, Y. Y.; Deacon, C.; Villada, A.; Cambell, R. C. J.; Sun, G.; Zhu, Y. G.; Feldmann, J.; Raab, A.; Zhao, F. J.; Islam, R.; Hossain, S.; Yanai, J. Geographical variation in total and inorganic arsenic content of polished (white) rice. *Environ. Sci. Technol.* **2009**, *43*, 1612-1617.

(10) Kile, M. L.; Houseman, E. A.; Breton, C. V.; Smith, T.; Quamruzzaman, O.; Rahman, M.; Mahiuddin, G.; Christiani, D. C. Dietary arsenic exposure in Bangladesh. *Environ. Health Persp.* **2007**, *115*, 889-893.

(11) Ohno, K.; Yanase, T.; Matsuo, Y.; Kimura, T.; Rahman, M. H.; Magara, Y.; Matsui, Y. Arsenic intake via water and food by a population living in an arsenic-affected area of Bangladesh. *Sci. Total Environ.* **2007**, *381*, 68-76.

(12) Mondal, D.; Polya, D. A. Rice is a major exposure route for arsenic in Chakdaha block, Nadia district, West Bengal, India: A probabilistic risk assessment. *Appl. Geochem.* **2008**, *23*, 2987–2998.

(13) Marin, A. R.; Masscheleyn, P. H.; Patrick, W. H. Soil redox-pH stability of arsenic species and its influence on arsenic uptake by rice. *Plant Soil* **1993**, *152*, 245-253.

(14) Takahashi, Y.; Minamikawa, R.; Hattori, K. H.; Kurishima, K.; Kihou, N.; Yuita, K. Arsenic behavior in paddy fields during the cycle of flooded and non-flooded periods. *Environ. Sci. Technol.* **2004**, *38*, 1038-1044.

(15) Xu, X. Y.; McGrath, S. P.; Meharg, A.; Zhao, F. J. Growing rice aerobically markedly decreases arsenic accumulation. *Environ. Sci. Technol.* **2008**, *42*, 5574–5579.

(16) Ma, J. F.; Yamaji, N.; Mitani, N.; Xu, X. Y.; Su, Y. H.; McGrath, S. P.; Zhao, F. J. Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. *Proc. Nat. Acad. Sci. U.S.A.* **2008**, *105*, 9931–9935.

(17) Su, Y. H.; McGrath, S. P.; Zhao, F. J. Rice is more efficient in arsenite uptake and translocation than wheat and barley. *Plant Soil* **2009**, in press.

(18) Li, R. Y.; Stroud, J. L.; Ma, J. F.; McGrath, S. P.; Zhao, F. J. Mitigation of arsenic accumulation in rice with water management and silicon fertilization. *Environ. Sci. Technol.* **2009**, *43*, 3778-3783.

(19) Norton, G. J.; Islam, M. R.; Deacon, C. M.; Zhao, F. J.; Stroud, J. L.; McGrath, S. P.; Islam, S.; Jahiruddin, M.; Feldmann, J.; Price, A. H.; Meharg, A. A. Identification of low inorganic and total grain arsenic rice cultivars from Bangladesh. *Environ. Sci. Technol.* **2009**, *43*, 6070–6075.

(20) Ma, L. Q.; Komar, K. M.; Tu, C.; Zhang, W. H.; Cai, Y.; Kennelley, E. D. A fern that hyperaccumulates arsenic. *Nature* **2001**, *409*, 579-579.

(21) Zhao, F. J.; Dunham, S. J.; McGrath, S. P. Arsenic hyperaccumulation by different fern species. *New Phytol.* **2002**, *156*, 27-31.

(22) Kertulis-Tartar, G. M.; Ma, L. Q.; Tu, C.; Chirenje, T. Phytoremediation of an arsenic-contaminated site using *Pteris vitrata* L.: A two-year study. *International Journal of Phytoremediation* **2006**, *8*, 311-322.

(23) Salido, A. L.; Hasty, K. L.; Lim, J. M.; Butcher, D. J. Phytoremediation of arsenic and lead in contaminated soil using Chinese Brake Ferns (*Pteris vittata*) and Indian mustard (*Brassica juncea*). *International Journal of Phytoremediation* **2003**, *5*, 89-103.