

(RESEARCH ARTICLE)



Metals in soil treated with gamma alumina-based nanomaterials. Retention and availability of aluminium, iron and nickel

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Abstract

Manufactured products containing nanomaterials based on metals increase continuously and can probably reach different environmental compartments. Soil contamination was evaluated through two experiments consisting on different methods (one using lysimeters and the other using a short method with agitation), developed under laboratory conditions. The lysimeters, which were long-term irrigated (for 121 or 142 days) with two different gamma alumina-based nanomaterials and the control ones, were disassembled and the soils analyzed. Some physicochemical characteristics and the concentration of Al, Fe and Ni were evaluated (Experiment A). On the other hand, the small-sample shaking method, designed solely to quantify soil contamination with metals, was carried out in search of a method requiring shorter periods of time (Experiment B) than those required by conventional methods using lysimeters. Finally, both methods were compared. Important retention of Ni from the nanomaterials was observed: 0.014 mg/g from 0.037 mg/g added as NiO-Al₂O to a lysimeter and 0.13 mg/g from 0.70 mg/g added as NiO-Al₂O or Ni-Al₂O₃ to the vessels used in the shaking method. The results lead us to conclude that the study through lysimeters allows evaluating the contamination of soil samples with nanomaterials and that the agitation method could probably be used in preliminary tests carried out before developing studies with lysimeters.

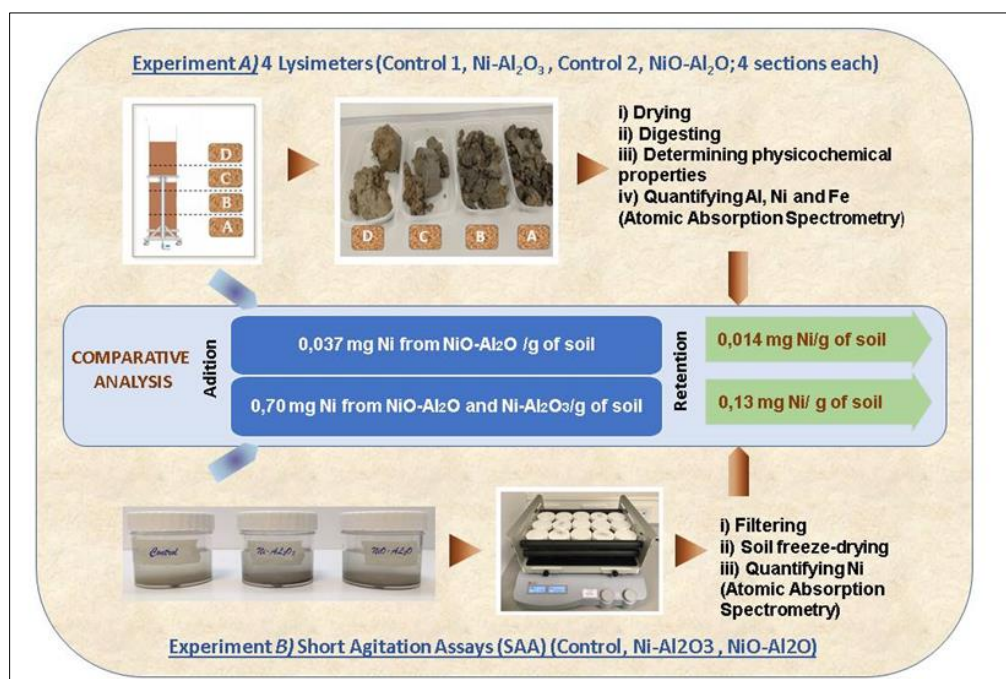
Keywords: Nanomaterials; Lysimeters; Metals quantification; Shaking method; Comparative analysis

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Graphical abstract



1 Introduction

Nanomaterials (NMs) are defined based on their length, which is less than 100 nanometers in at least one of their dimensions. There is a continual increase in the number of commercially available products. Their uses include health care, electronics, cosmetics, textile products, information technology, environmental care and others. NMs have different properties than the non-nanometric material due to their small size and large surface area [1]. For these reasons, it is absolutely necessary to evaluate their possible effects, since they can be toxic to a wide variety of organisms. Among the most widely used NMs are metal oxides, such as nickel oxide (NiO). Some of them, which contain Alumina (Al₂O₃) and Ni, due to their thermal stability and high surface area, are widely used as supports in heterogeneous catalysis processes. The industry provides information on the presence of NMs obtained by chemical synthesis in various products. However, there is still limited information on the use of some products and practically no information on the final disposal of the waste that contains them.

The study of the presence and fate of NMs in water, soil and sediments is of great importance due to the impact that these materials can have on them [2,3]. Theoretical developments describing the behaviour of particles and chemicals in the environment are rarely applicable to NMs, as their behaviour in environmental compartments depends both on their own properties and the properties of the place where they are disposed of.

Living organisms can incorporate NMs by breathing, feeding, or through plant roots [4]. The organisms that live in soil or sediment can bioaccumulate NMs [5]. Furthermore, their concentration could probably increase at higher levels of the food chain, due to magnification processes [4]. The increasing use of NMs in industry is likely to lead to their deposition in these compartments, thus it is of great importance to study the fate of NMs in them. The main objective of the present study was to evaluate different methods to estimate the fate of different gamma alumina-based NMs when disposed of in the soil. Soil samples from the Province of Chubut, Argentina, were used in two different trials: a study through lysimeters that were irrigated with NMs and a shorter experiment, using less amount of soil, by adding NMs and non-NM metals, under constant shaking.

The particular objectives were:

- The evaluation of the retention and availability of Ni and Al deposited as NM suspensions on top of the lysimeters and Fe as a metal already present in the soil matrix, according to its importance as a nutrient for living organisms.
- The study of different soil properties of treated and Control lysimeters, at the end of the treatments.

- The quantification of Ni retention when the metal was added in the form of a saline solution or as part of suspensions of NMs containing Ni, in experiments carried out by stirring the soil in small containers.
- The analysis of advantages and disadvantages of the methods described above.

2 Material and methods

- A) The physical and chemical parameters of the soil were analyzed from lysimeters of 4 kg each. Two devices were irrigated for 121 days with deionized water (Control 1) and a suspension of NM at 100 mg/L ($\text{Ni-Al}_2\text{O}_3$) and another two ones for 142 days with deionized water (Control 2) and with another NM suspension at 100 mg/L ($\text{NiO-Al}_2\text{O}$). At the end of these periods, each lysimeter was disassembled and divided into four sections called A, B, C and D from bottom to top. Then, the samples were dried during 15 days at room temperature and the following evaluations were made: moisture content ; total carbon (TC) ; organic carbon (OC) ; granulometry; Al and Ni retained and Fe already present, by acid digestion and atomic absorption spectrometry and bioavailability of Al, Ni and Fe, by extraction with NH_4^+Ac^- at pH = 5.5 and atomic absorption spectrometry.
- B) A separate experiment was carried out to evaluate metal retention in the soil as a possible alternative and predictive method, through Short Agitation Assays (SAA). Fine tuning of Ni retention after 24 hours of stirring was carried out using different concentrations of Ni from a $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ solution (0.44, 0.86, 2.30, 4.78 and 9.88 mg/L, quantified by atomic absorption spectrometry). At the end of the treatments, the samples were filtered and the concentration of Ni in the supernatants was measured through atomic absorption spectrometry. The concentration of Ni in the soil matrices was estimated in the filtrates by calculating the differences against the concentration of Ni in the solutions applied in each container. Subsequently, another assay was carried out with suspensions of NM at 100 mg/L ($\text{Ni-Al}_2\text{O}_3$ and $\text{NiO-Al}_2\text{O}$) and Control soil at different exposure times ($t = 2, 5, 12, 19$ and 30 days). All containers contained 2 g of soil and 50 mL of each solution or suspension. At the end of the treatments, the soils were lyophilized and Ni concentration was evaluated in aliquots previously digested, through atomic absorption spectrometry.

Both experiments, A and B, were carried out in our laboratories under a photoperiod of 12 hours and 24°C.

3 Results and discussion

The physical and chemical properties of the four sections of each lysimeter, first analyzed separately, were averaged due to the little difference observed between the results, which were previously discussed [6]. The moisture content only showed a significant difference ($p < 0.0073$) between the $\text{NiO-Al}_2\text{O}$ lysimeter (33.00 % \pm 0.65 %) and the value of Control 2 (31.20 % \pm 0.63 %). The TC means did not show significant differences between the lysimeters Control 1 and $\text{Ni-Al}_2\text{O}_3$ or Control 2 and $\text{NiO-Al}_2\text{O}$. The four values of TC were between 0.77 g/100 g of soil and 0.80 g/100 g of soil. In line with TC, the means of OC results did not show significant differences between Control 1 and $\text{Ni-Al}_2\text{O}_3$ or Control 2 and $\text{NiO-Al}_2\text{O}$ lysimeters and were between 0.20 g/100 g of soil and 0.23 g/100 g of soil.

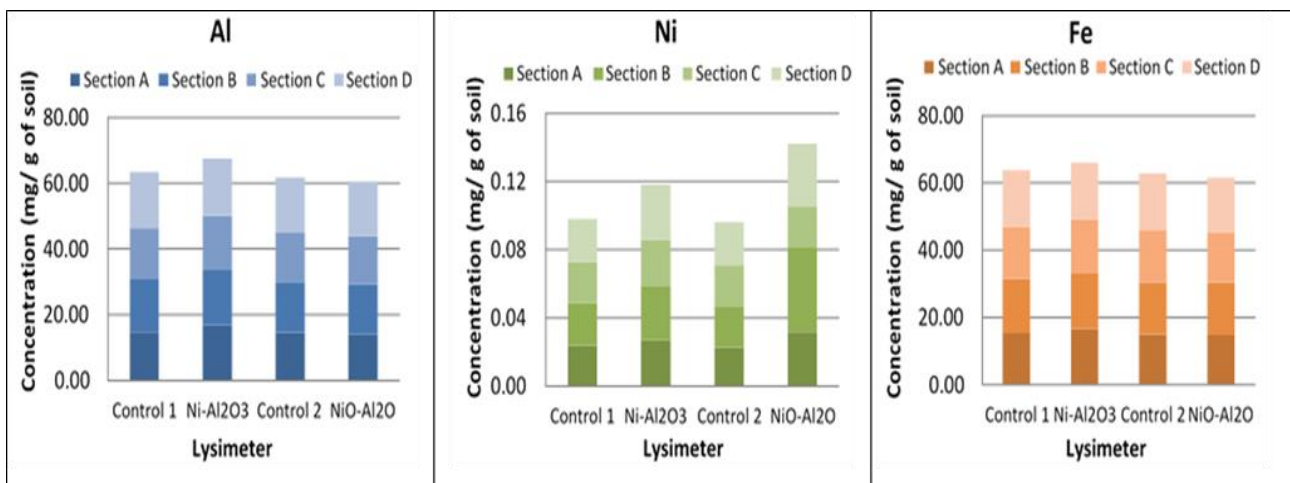


Figure 1 Total concentration of Al, Ni and Fe in the four sections of the lysimeters soil, expressed as mg/g of soil

Particle size analysis of soils showed a homogeneous distribution in all sections of the lysimeters and predominant composition of 50 to 55% of fine sand fraction (88 μm in diameter).

The concentration of metals in each section of all the lysimeters can be seen in figure 1. The soil Al and Fe concentration increased slightly in some sections of the lysimeter treated with Ni-Al₂O₃ when compared to its Control (6.0% and 3.47% respectively in the set of stacked concentrations). On the other hand, the same analysis showed that Ni sets of stacked concentrations increased 16.67% and 28.7% in the lysimeters treated with Ni-Al₂O₃ and NiO-Al₂O compared to their respective Controls.

Figure 2 shows that both Al and Fe were bioavailable in three lysimeters but not in the one irrigated with Ni-Al₂O₃, in contrast with the results published by Fonovich et al. [3]. More experiments should be performed, probably under different protocols, to exclusively analyse the bioavailability of Al and Fe. An interesting comparison can be made between the bioavailability of Ni and its retention. It can be seen that, despite the observed retention of Ni added to the treated lysimeters, its bioavailability could not be clearly differentiated from that of the Controls. Therefore, this metal would possibly have to be present in the NM forms in the soil for longer periods, not only to be retained but also to be available to a different degree compared to the control lysimeters.

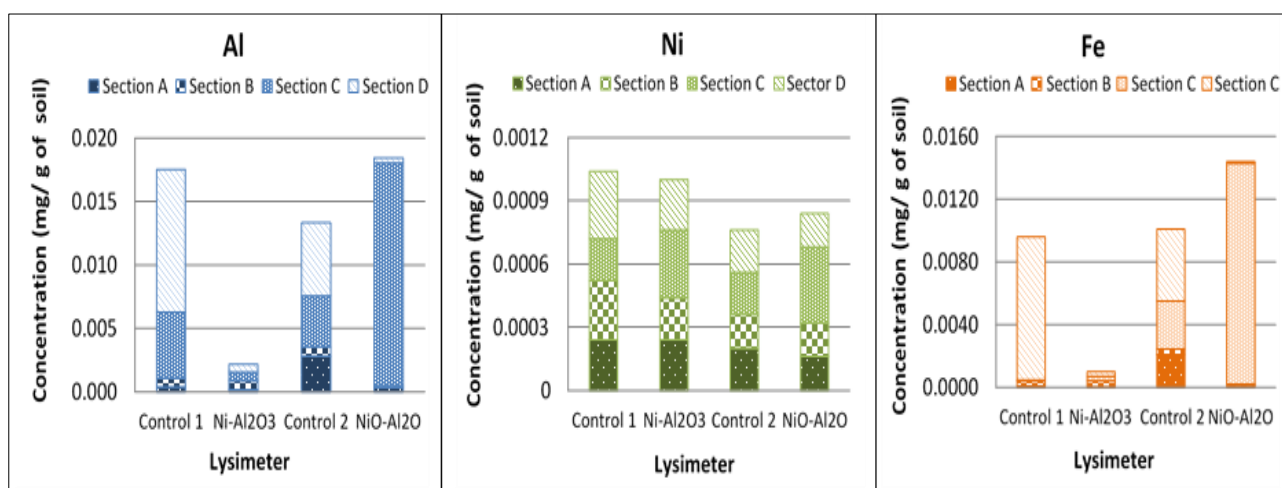


Figure 2 Bioavailable concentration of Al, Ni and Fe in the four sections of the lysimeters, expressed as mg/g of soil

The results of SAA test carried out with Ni (NO₃)₂·6 H₂O solutions at different concentrations for 24 hours, demonstrated the linear response of the method for Ni (figure 3A). Figure 3B shows the results of SAA test carried out with NMs. Ni was retained in both NMs tested and Ni concentration could be clearly distinguished between treated and control devices. More studies should be done to choose the best time period and possible saturation concentration for each of these materials in SAA.

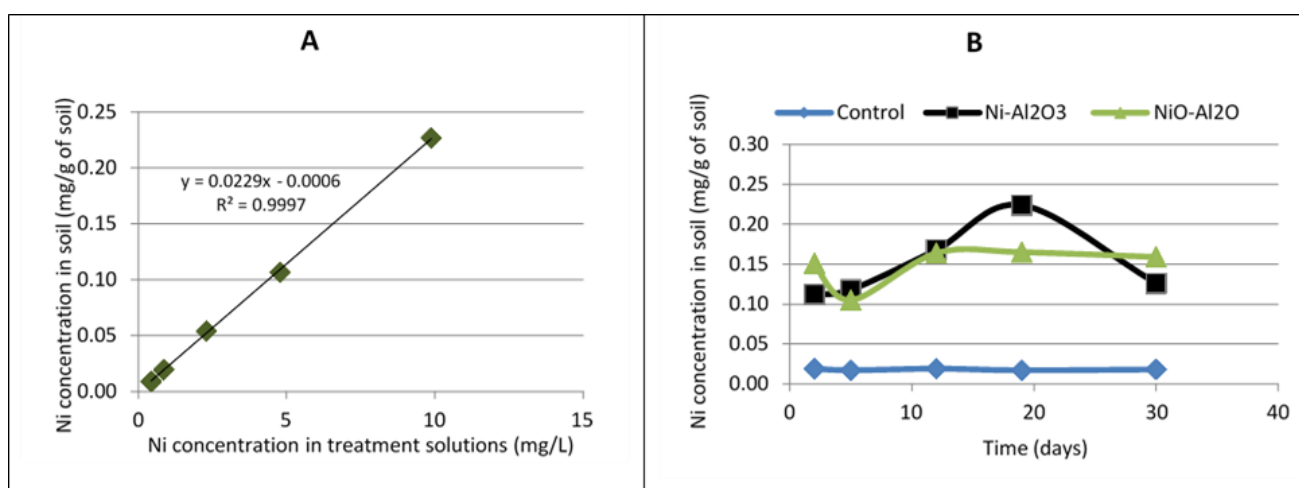


Figure 3 A) Ni concentration retained in the soil versus Ni concentration in Ni (NO₃)₂·6 H₂O treatment solutions. SAA protocol performed with Ni in the form of saline. B) Total Concentration of Ni in soil as a function of exposure time. SAA protocol performed with NMs containing Ni

Table 1 shows the mean concentrations and important retention of Ni, expressed in the final column as % of the metal added to the soil in both experiments, A and B. Retained metal concentration (third column) was calculated for each lysimeter considering the sum of Ni amounts in all the sections and the total weight of the soil. The possible conflict that arises when comparing this analysis with figure 1A for the lysimeter treated with Ni-Al₂O₃ is due to its irregular dissection and the calculation performed. It can be observed that Ni concentration after addition of both NMs in SAA was 0.130 mg/g of soil in contrast to the guide value of 0.100 mg/g of soil, recommended in Law number 24051 for Hazardous Wastes in residential soil in Argentina.

Table 1 Comparative analysis of the concentration of Ni added and retained in the soil of different tests and Ni retention %, for additions made in the form of NMs both in SAA and lysimeter experiments

Assay	NM	Ni added (mg/g of soil)	Retained Ni (added - already present) (mg/g of soil)	Retained Ni in soil/Ni added to soil (%)
SAA	Ni-Al ₂ O ₃	0.700	0.13 ± 0.05	18.80 ± 6.77
SAA	NiO-Al ₂ O	0.700	0.13 ± 0.02	18.69 ± 3.52
Lysimeter	Ni-Al ₂ O ₃	0.039	0.001	3.86
Lysimeter	NiO-Al ₂ O	0.037	0.014	38.51

It has been reported by different authors that Ni from NMs entering the soil could probably affect not only the growth of different wild species but also the quality of the resource and human health [7,8]. Future studies along the lines of this work would be complementary to reach a precise understanding of the behaviour of the NMs in this environmental compartment in the field, as well as their effects on living organisms.

4 Conclusion

The present work confirms the usefulness of lysimeters to quantify the retention of Ni deposited in the soil, under laboratory conditions, but not to differentiate the concentration of Al added from that existing in the matrix, due to the high amounts of Al already present. SAA was designed exclusively in our laboratory for the quantification of Ni and the preliminary results obtained confirm its suitability for this purpose.

The results obtained from short assays with agitation (SAA) can be useful to predict the need for future longer and more expensive evaluations with lysimeters.

It can also be pointed out that the entry of NMs in punctual specific sites (deposition of waste on the ground without treatment) can contribute to raising the Ni concentration, which could eventually reach values above the maximum established by the corresponding regulations.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

There was no conflict of interest.

References

- [1] Perez-Catán S, Guraya MM. High porous gamma-alumina synthesized by a modified sol-gel technique. *International Journal of Material Science and Engineering*. 2015; 5(2): 33-39.
- [2] Scientific Committee on Emerging and Newly-Identified Health Risks (SCENIHR). The appropriateness of the risk assessment methodology in accordance with the Technical Guidance Documents for new and existing substances

for assessing the risks of nanomaterials [internet]. Brussels: Health & Consumer Protection, Directorate-General. 2007.

Available from https://ec.europa.eu/health/ph_risk/committees/04_scenihhr/docs/scenihhr_o_010.pdf

- [3] Fonovich TM, Pérez Coll CS, Blanco Bermudez L, Guraya M, Cappari G, Perez Catán S. Fate of aluminium and nickel in soil. Evaluation through lysimeters under laboratory conditions. *Soil and Sediment Contamination: An International Journal*. 2021; 30(2): 187-200.
- [4] Scientific Committee on Emerging and Newly-Identified Health Risks (SCENIHR). Risk Assessment of Products of Nanotechnologies [internet]. Brussels: Health & Consumer Protection, Directorate-General. 2009. Available from https://ec.europa.eu/health/ph_risk/committees/04_scenihhr/docs/scenihhr_o_023.pdf
- [5] Klaine SJ, Alvarez PJ, Batley GE, Fernandes TF, Handy RD, Lyon DY, Mahendra S, McLaughlin MJ, Lead JR. Nanomaterials in the environment: behavior, fate, bioavailability, and effects. *Environmental Toxicology and Chemistry: An International Journal*. 2008; 27(9): 1825-1851.
- [6] Bardi HM. Treatment of soil with metals from gamma alumina-based nanomaterials. Retention and availability of aluminium, iron and Nickel [Bachelor Thesis] San Martín, Argentina: National University of San Martín. 2020.
- [7] Henderson RG, Durando J, Oller AR, Merkel DJ, Marone PA, Bates HK. Acute oral toxicity of nickel compounds. *Regulatory Toxicology and Pharmacology*. 2012; 62(3): 425-432.
- [8] Shahzad B, Tanveer M, Rehman A, Cheema SA, Fahad S, Rehman S, Sharma A. Nickel; whether toxic or essential for plants and environment-A review. *Plant Physiology and Biochemistry*. 2018; 132: 641-651.