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Effects of Different In Situ Remediation Strategies for an As-Polluted Soil on Human Health Risk, Soil Properties, and Vegetation

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Abstract: The demand for soils for recreational uses, gardening, or others in urban and periurban areas is increasing, and thus the presence of polluted technosols in these areas requires nature-based in situ remediation technologies. In this context, the capacity of three amendments, namely zero valent iron nanoparticles (nZVI), compost and a mixture of compost and biochar, to immobilise As in a polluted technosol simultaneously cultivated with *Lolium perenne* L. were tested and compared. The characteristics of the soil were comprehensively characterised by chemical and X-ray analysis to determine As contents, distribution, and mineralogy. As mobility was evaluated by the RBA methodology and then potential human health risks, both carcinogenic and non-carcinogenic, were assessed in all treatments. The nZVI treatment reduced risks due to the As immobilisation obtained (41% As decrease, RBA test), whereas the organic amendments did not imply any significant reduction of the RBA values. As to soil properties, the organic treatments applied lowered the pH values, increasing cation exchange capacity, and carbon and nutrient contents. To determine impacts over plant production, fresh biomass, As, Ca, Fe, K, Mg, Na and P were measured in *Lolium* under the different treatments. Notably, organic amendments improved As extraction by plants (57% increase), as well as fresh biomass (56% increase). On the contrary, nZVI diminished As extraction (65% decrease) and promoted a fresh biomass decrease of 57% due to nutrients immobilisation (61% decrease of P in plants tissues).

Keywords: technosol; nanoremediation; compost; biochar; phytoremediation; risk assessment

1. Introduction

The increase of urban sprawling is a common phenomenon in recent decades due to the rapid urban population growth [1]. This implies various anthropogenic activities including industrial operations, municipal processes, urban gardening, and construction among others, which may affect soil quality [2]. Consequently, in many cases, soils allocated in urban and periurban areas became technosols [3] thereby acquiring several problematics, such as an increased concentration of metal(loid)s, which requires attention regarding human health risks [4–6]. This is partly explained because, unlike natural soils, technosols typically contain materials such as slags, clinker, ashes, and construction debris, which often carry a significant metal (loid) contamination [7,8]. Due to this alteration, a thorough risk assessment is usually necessary to select remediation approaches taking into account future soil uses and the reduction of threats to human health and the environment [9].

One of the most common and hazardous soil contaminants is arsenic (As). In fact, As contamination is a widespread problem because of its negative impact on living organisms and human health [10].

This metalloid usually appears in urban-type technosols and represents a severe threat because of its potential accumulation in the human food chain, essentially by plant uptake and animal transfer [11]. This could affect human health given the carcinogenic and toxic character of As [12]. Furthermore, different precautions should be taken into account when treating soil due to the anionic form of this metalloid [13–15].

Nature-based solutions (NBS) is an umbrella concept used to apprehend nature-based, cost-effective and eco-friendly treatment technologies, as well as redevelopment strategies that are socially inclusive, economically viable, and with good public acceptance [16]. The NBS can offer a great variety of benefits, ranging from less energy usage and higher material efficiency to increased resilience to global environmental change [17,18]. Therefore, these technologies are very suitable for soil treatment in urban and peri-urban areas. Some of the proposed nature-based remediation technologies, all of them applicable to As pollution, are phytoremediation, bioremediation, stabilisation with amendments such as biochar, green mulch or compost, and nanoremediation [16–20].

Currently, there are two main NBS trends to treat soils contaminated with metal(loid)s, such as As [20]. The first one consists of the immobilisation of the metal(loid)s in the soil trying to avoid the As enter into the trophic chain. For this purpose, the selection of amendments is critical, and it is done according to the metal(loid) to be immobilised [14]. In the case of As immobilisation, nanoremediation is a modern technology [21] that is beginning to be used through the application of zero valent iron nanoparticles (nZVI). This technology has already provided good results in water [10,22] and soils [23–25], even at field scale [26]. The second approach for As-polluted soil remediation consists on the mobilisation of the contaminant so that it can be progressively removed by means of sustainable techniques such as phytoextraction, alone or combined with the application of organic soil amendments [27,28]. As several authors demonstrated, the organic amendments (compost, biochar) due to their negative surface charge and dissolved organic carbon mobilise As [14,15,29,30], facilitating the capture of As in soil solution by phytoextraction plant species and thus, favouring its accumulation in biomass [31]. Consequently, this process would lead to a gradual decrease in the available As concentration in soil [28]. Also, the use of phytoremediation combined with amendments made with by-products is concordant with circular economy principles [32]. Within the potential As-phytoextracting plants reported by several authors, Li et al. [33] demonstrated that *Lolium perenne* L. can grow under the stress caused by high concentrations of As. *Lolium perenne* L. was also used for As phytoremediation by Clemente et al. [27], while Karczewska et al. [34] evaluated the effects of different amendments on its growth.

Following the preceding considerations, the main objective of this work is to test the two aforementioned strategies, mobilisation and immobilisation, in an As-polluted technosol located in the surroundings of a peri-urban area. This work compares an inorganic treatment (nZVI) to decrease As mobility, which could affect negatively plant development and soil properties, with two organic treatments, compost and biochar, which can improve plant development and soil quality, although they can mobilise the As. The potential reduction of human health risks, the amelioration of soil properties, and the reduction/increase of the incorporation of As into the trophic chain were examined.

2. Materials and Methods

2.1. Soil Sampling and Characterisation

The technosol sampled in this study is located in a periurban area of the municipality of Madrid, Spain, which according to the land use planning, will be harnessed in the future for residential use. Initial analyses of several soil samples (data not shown) revealed As concentration exceeding the Soil Screening Levels in force for the urban and industrial land uses (24 and 40 mg·kg⁻¹ respectively) [35]. To characterise the technosol, a composite representative sample of 20 kg was obtained, air-dried and sieved through 2 mm mesh. After homogenisation, subsamples were obtained with an aluminium riffler and subjected to the following analyses according to [36]: Soil pH was determined using a pH

electrode in a water to soil extract of 1:2.5. The quantitative determination of organic matter was carried out by dry route by difference in weight after a 24 hour combustion in a muffle at 550 °C, whereas available P was determined by Mehlich 3 method, and total nitrogen (TN) content was quantified by the Kjeldahl method. Pseudo-total As concentration was measured by ICP-MS (7700 Agilent Technologies equipment) after extraction using aqua regia by acid digestion in a microwave oven (Milestone ETHOS 1, Italy). Ca, K, Mg, Na, Al, and exchangeable cations (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , Al^{3+}) were extracted with 0.1 M BaCl_2 , and ICP-MS determined element concentrations. Effective cation exchange capacity (CEC) was calculated using the sum of exchangeable cation concentrations.

Subsamples above 2 mm were also observed using a Dino-Lite Digital Microscope to obtain preliminary mineralogical data. To corroborate the microscopy study, they were also studied by X-ray diffraction (XRD) using a Phillips X' Pert Pro diffractometer with Cu $\kappa\alpha 1$ radiation (1.540598 Å); after determining the position of Bragg peaks observed over the range of $2\theta = 5\text{--}90^\circ$, the minerals were identified using databases of the International Centre for Diffraction Data. Furthermore, the major compounds of the soil were measured using X-ray fluorescence (XRF) employing a Philips PW2404 X-ray fluorescence spectrometer. Both XRD and XRF were carried out after grounding materials above 2 mm to ensure the homogeneity of the rock sample. Finally, grain size distribution of the fraction below 2 mm was determined by wet-sieving (ASTM D-422-63, Standard Test Method for Particle Size Analysis of Soils) in order to obtain the different soil fractions (2000–1000, 1000–500, 500–250, 250–125, 125–63, <63 microns). Subsequently As contents in the different fractions were determined by ICP-MS after acid digestion as described above.

2.2. Organic and Inorganic Amendments

The compost (C) used was made from animal manure mixed with plant debris and provided by Piensos Lago S.L. (Asturias, Spain). Biochar (B), which was provided by PYREG Carbon Technology Solutions (Dörth, Germany), was made from wood (remains of pruning) following the PYREG® methodology. Parameters studied in organic amendments were the same as in soil samples (see above), excluding mineralogy and grain size studies; i.e., EC, pH, total carbon, nitrogen, available phosphorus, pseudo-total concentrations (As, Cd, Cu, Pb, Zn), available concentrations of As, nutrients (Ca, K, Mg, Na, Al) and cation exchange capacity.

ZVI nanoparticles (nZVI), namely NANOFER 25S, were supplied by NANO IRON s.r.o. (Brno, Czech Republic). According to commercial specifications, this product has an iron content of 14–18%, and 2–6% of magnetite. The particles have an average size of around 60 nm, the suspension is strongly alkaline (pH 11–12), and the active surface area is 20 m²/g (additional details are available at www.nanoiron.cz). These nanoparticles were deeply characterised in previous works [37], revealing that the zeta potential of nZVI was negative due to the polyacrylic acid (PAA) used as a coating to stabilise the nanoparticles and prevent agglomeration.

2.3. *Lolium perenne* L.

Lolium perenne L. seeds, supplied by Piensos Lago S.L. (Asturias, Spain), were sown in pots, which were watered to field capacity throughout the experiment. *Lolium perenne* L. was grown in all pots for 30 days.

2.4. Greenhouse Experiment and Monitoring

The one-month experiment was performed in a greenhouse where twelve plant pots, three per treatment, were prepared and distributed randomly in the greenhouse. Non-amended pots containing only the polluted soil (S) were used as controls. Three treatments were chosen, the first (SN) consisted of the application of nZVI in order to know if just the decrease in As concentration in the soil is sufficient to improve soil conditions and to allow a proper vegetation growth. In the second treatment, two organic treatments were chosen. One of them (SC treatment) consisted of compost application, which has been shown to improve soil conditions for plant development but may increase As mobility [13].

The second organic treatment (SCB) was carried out by a blend of compost and biochar since biochar can foster the positive effects of compost. It must be noted that according to several authors, this latter procedure, can decrease As mobility, whereas according to others, it can enhance it [30,38]. The amendments were mixed with the polluted soil up to 0.5 kg per pot. The dose of nZVI suspension applied to the soil was 2.5%, based on prior works with As-polluted soils [26,31,37,39,40]. In the case of SC and SCB treatments, the proportions were 12.5% of compost and 2.5% of biochar (Table 1). These doses were based on previous works with similar treatments [41–43].

Table 1. Doses and amendments applied in each treatment (% weight).

Treatment	Soil	nZVI	Compost	Biochar
S	100			
SN	97.5	2.5		
SC	87.5		12.5	
SCB	85		12.5	2.5

nZVI: Zero valent iron nanoparticles.

Throughout the experiment, greenhouse average temperature was maintained at 13 ± 4 °C, and pots were watered to field capacity, while plant growth was supervised under visual examination to detect toxicological effects. After the incubation time, the pots were dismantled, the aerial part was harvested, and the soil samples were air-dried and sieved through a 2 mm mesh. Soil pH, organic matter, available P, pseudo-total As concentration, As RBA extraction, exchangeable cations (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , Al^{3+}) were determined following the procedures described above.

Also, at the end of the experimental time, plant biomass was measured on harvested *Lolium perenne* L. plants. The biomass was carefully washed with deionised water, immediately weighed, and dry mass was determined after oven-drying for 48 h at 80 °C and cooling at room temperature. As, P, Na, Mg, K, Ca, and Fe contents were determined by ICP-MS after, digestion in a microwave oven (Milestone ETHOS 1, Italy. 1600W, 30 min) using 0.2 g sample and 12 ml of HNO_3 .

2.5. As Assessment by RBA Extraction

For determining the oral available As, the Solubility/Bioavailability Research Consortium (SRBC) test was performed according to Kelley et al. [44] and Juhasz et al. [45]. The method consists on a simple extraction at low pH simulating the gastric liquids; thus soil subsamples of 1 gram with grain size smaller than 250 microns, obtained by sieving, were mixed with a solution of 30.03 g/L glycine at pH 1.5 following a relation 1:100 (w:v). The mixture was shaken at 40 rpm for 1 h at 37 °C, and then samples were centrifuged, and the supernatant was filtered at 0.45 microns before As analysis by ICP-MS. The RBA (Relative Bioavailability factor) value was then calculated by the ratio between this oral available As concentration and the As pseudo–total concentration.

2.6. Human Health Risk Assessment

Risk assessment was done following the USEPA methodology [46], as recommended by regulations in most European countries, and specifically in Spain [47]. Initially, and taking into account the planned near future land use of the site, the site–specific exposure scenario corresponds with a residential one. In this context, the most sensitive human receptors to be considered are children.

The Average Daily Dose for ingestion exposure (ADD, expressed in $\text{mg}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$), according to USEPA [48], is determined by means of Equation (1):

$$ADD = \frac{CS \times IR \times EF \times RBA \times CF}{BW \times AT} \quad (1)$$

where:

- *CS*: As concentration in soil ($\text{mg}\cdot\text{kg}^{-1}$). This value depends on the soil treatment.
- *IR*: daily ingestion rate ($\text{mg}\cdot\text{d}^{-1}$). For children, this value is $200 \text{ mg}\cdot\text{d}^{-1}$ [46].
- *EF*: exposure frequency ($\text{d}\cdot\text{a}^{-1}$). This value is $350 \text{ d}\cdot\text{a}^{-1}$ [49].
- *RBA*: relative bioavailability factor (adimensional). This value depends on the soil treatment.
- *CF*: conversion factor ($10^{-6} \text{ kg}\cdot\text{mg}^{-1}$).
- *ED*: exposure duration (years). For children, this value is 6 years [46].
- *BW*: average body weight (kg). For children, this value is 15 kg [48].
- *AT*: averaging time (days). This value is equal to exposure duration (*ED*) for non-carcinogens risk analysis and 70 years for carcinogens risk analysis [49].

To quantify the risk, the calculation was divided into two categories: non-carcinogenic risk and carcinogenic risk. The potential non-carcinogenic risk is defined by the hazard index (*HI*), which was determined for As by means of Equation (2):

$$HI = \frac{ADD}{RfD} \quad (2)$$

where *RfD* is the oral reference dose for As, $3 \times 10^{-4} \text{ mg}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$ [49]. In this regard, when the *HI* is below 1, it is considered that there is no toxicological risk [46].

On the other hand, the carcinogenic risk (*CR*) due to As is determined as:

$$CR = \frac{ADD}{SF} \quad (3)$$

where *SF* is the slope factor ($\text{kg}\cdot\text{d}\cdot\text{mg}^{-1}$), provided for As by US EPA [50] with a value of $1.5 \text{ kg}\cdot\text{d}\cdot\text{mg}^{-1}$. According to US EPA, *CR* values lower than 10^{-6} imply that risk is so small as to be negligible; from 10^{-6} to 10^{-4} , the risk is tolerable; and if *CR* is higher than 10^{-4} , the risk becomes unacceptable (1 person among 10,000 is in risk of developing cancer); nevertheless, in Spain the regulations in force [47] established 10^{-5} as the threshold to consider unacceptable risks.

2.7. Statistical Analysis

All analytical determinations were performed in triplicate. The data obtained were statistically treated using the SPSS programme, version 24.0 for Windows. Analysis of variance (ANOVA) and the test of homogeneity of variance were carried out. In the case of homogeneity, a post hoc least significant difference (LSD) test was done. If there was no homogeneity, Dunnett's T3 test was performed. Bivariate analysis was also carried out by means of Pearson correlation.

3. Results and Discussion

3.1. Soil and Amendments Characterisation

The characterisation of the soil and the amendments is summarised in Table 2. Soil properties assessment revealed a silty and alkaline poor soil with low organic matter, low nitrogen and low phosphorus content and high Ca and Mg contents. The initial As concentration in the soil is $76 \text{ mg}\cdot\text{kg}^{-1}$, exceeding the Soil Screening Level (SSL) of the community of Madrid for residential land uses ($24 \text{ mg}\cdot\text{kg}^{-1}$), although the available fraction using RBA is quite lower, near to $8 \text{ mg}\cdot\text{kg}^{-1}$. Regarding the other potentially toxic elements, the concentrations were below the current regulation levels. Soil mineralogy, according to XRD results, is formed by calcite as the main phase, and dolomite and quartz as secondary minerals; these data are in accordance with the high Ca and Mg contents in the soil. After microscopy observations of the grains coarser than 2 mm, the rock was classified as marl, which was confirmed by an XRF analysis (Table S1). The relevant percentage of iron oxide (above 5%) suggests that As might be associated with this soil component, which could explain the relatively low As availability mentioned above [14,51].

The grain size analysis of the fraction below 2 mm revealed that As concentration is higher in the finest fraction (<63 microns), which represents 60% of the soil and as a consequence As recovery in the finest fraction is 76% (Table S2). However, in the other fractions, As contents are above the SSL, and therefore a soil size-fractionation approach to reduce polluted soil volume was ruled out.

As regards amendments characterisation, the compost selected showed an alkaline pH and high electrical conductivity due to the high concentrations of nutrients, mainly K (Table 2). In contrast, the total carbon and phosphorus content is higher than in the soil, which is in accordance with a typical compost composition. The As concentration in the compost and the biochar are remarkable, although not so much relevant due to the negligible available As concentration. On the other hand, biochar is revealed as an alkaline material with very high organic matter content, high P and K contents, and also high electrical conductivity.

Table 2. Polluted soil (S), compost (C) and biochar (B) characteristics.

Parameters		Units	S	C	B
Physic-chemical properties	EC	$\mu\text{s}\cdot\text{cm}^{-1}$	111 \pm 1.00c	11,911 \pm 3.60a	642 \pm 1.03b
	pH		8.70 \pm 0.02b	8.07 \pm 0.01c	9.65 \pm 0.03a
	OM	$\text{mg}\cdot\text{kg}^{-1}$	2.28 \pm 0.03c	177 \pm 0.53b	713 \pm 0.73a
	TN		2.16 \pm 0.20c	12.41 \pm 0.02a	9.60 \pm 0.02b
	P (available)		1.73 \pm 0.03c	1656 \pm 4.96a	161 \pm 0.72b
Pseudo-total	As		76.3 \pm 0.43a	22.4 \pm 0.49b	14.6 \pm 0.52c
	Cd		u.l	1.51 \pm 0.01a	0.75 \pm 0.01b
	Cu	$\text{mg}\cdot\text{kg}^{-1}$	29.1 \pm 0.40b	33.6 \pm 0.57a	15.7 \pm 0.43c
	Pb		37.9 \pm 0.06b	29.3 \pm 0.05c	40.6 \pm 0.15a
	Zn		120 \pm 0.56c	148 \pm 1.30b	221 \pm 0.16a
RBA	As	$\text{mg}\cdot\text{kg}^{-1}$	7.61 \pm 0.45a	0.65 \pm 0.02b	0.10 \pm 0.01c
Nutrients	Ca	$\text{mg}\cdot\text{kg}^{-1}$	2685 \pm 149b	6337 \pm 9.36a	756 \pm 2.86c
	K		315 \pm 30.10c	18,127 \pm 2.50a	2554 \pm 1.36b
	Mg		1013 \pm 138b	1657 \pm 2.06a	26.7 \pm 0.03c
	Na		51.5 \pm 7.66c	3412 \pm 2.25a	140 \pm 0.51b
Exchange cations	Al	$\text{cmol}_{(+)}\text{kg}^{-1}$	0.03 \pm 0.00a	0.01 \pm 0.00a	0.33 \pm 0.40a
	Ca		44.1 \pm 2.82b	63.6 \pm 0.53a	7.52 \pm 0.49c
	K		2.60 \pm 0.27c	92.6 \pm 0.40a	13.5 \pm 0.46b
	Mg		28.7 \pm 3.28a	27.5 \pm 0.35a	0.44 \pm 0.01b
	Na		1.46 \pm 0.16b	34.3 \pm 0.50a	1.40 \pm 0.01b
	CEC	$\text{cmol}_{(+)}\text{kg}^{-1}$	76.9 \pm 5.85b	217 \pm 2.17a	22.3 \pm 0.33c
Texture	Lime		26.2		
	Sand	%	33.1		
	Silt		40.7		

For each row, different letters in different samples mean significant differences ($n = 3$, ANOVA; $p < 0.05$). u.l. undetectable level. Typical deviation is represented by \pm .

3.2. Arsenic in Soils and Human Health Risk Analysis

The applied treatments did not cause a significant variation in the pseudo-total concentration of As (Figure 1A). However, the soil treated with the inorganic amendment (SN, nZVI nanoparticles) revealed a significant decrease in the available As concentration (Figure 1B). The application of the SN treatment in As-polluted soils has been studied in previous works revealing excellent performance for As immobilisation [37]. The main mechanism is the As sorption in the surface of the nanoparticles via inner-sphere surface complexation onto the iron oxides of the shell surrounding the nZVI [26,37,39,40].

The percentage of available As concentration over the pseudo-total As concentration represents the RBA factor, which is critical for risk analysis. This factor, represented in Figure 1C, reveals the

same effect that the available As concentration, decreasing only in the case of the SN treatment (nZVI treatment).

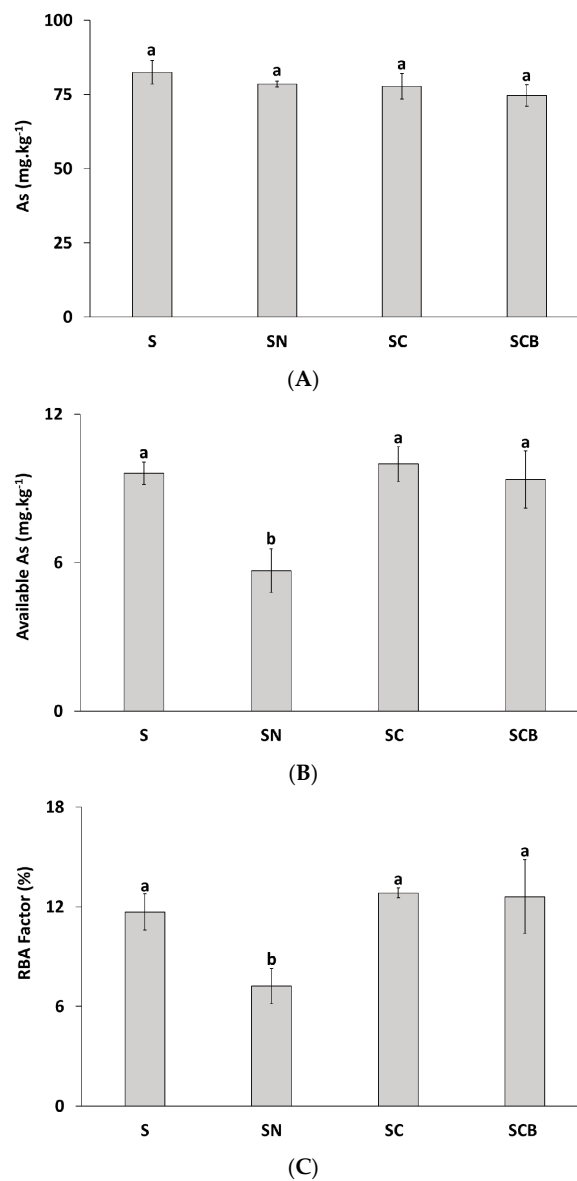


Figure 1. Pseudo-total As concentration (A), available As concentration (B) and RBA factor (C) in the polluted soil (S) and in the treated soil with nZVI (SN), compost (SC) and compost-biochar (SCB). For each column, different letters in different samples indicate significant differences ($n = 3$, ANOVA; $P < 0.05$).

The carcinogenic and non-carcinogenic ADD for children living in the site was determined taking into account the different scenarios: polluted soil, nZVI-treated soil, compost treated soil and compost-biochar treated soil (Table 3). These values were similar, except for the nZVI-treated soil (SN) which displayed lower figures. Therefore, after nZVI application, HI decreased by 44%, whereas after organic amendments, did not alter it significantly (Table 3). However, despite the toxicity of As, in this case, the risk is below than 1. Additionally, concerning the carcinogenicity of As, CR was also determined (Table 3). In all cases the CR is lower than 10^{-6} although very close to that threshold, with the only exception of the nZVI treatment (SN) which resulted in a notably lower CR value than the other experiments (S, SC, and SCB). On the whole, the nZVI treatment was very effective to diminish risk values as a direct consequence of the RBA reduction observed in Figure 1, on the contrary the

organic amendments did not alter significantly HI and CR values when compared with the control experiment. This suggests that a complimentary effect of both amendments could be obtained in a combined application given that (see below) the organic amendments have a better performance in improving soil properties and favouring plant growth.

Table 3. Human health risk analysis for the polluted soil (S) and soil after treatments application with nZVI (SN), compost (SC) and compost-biochar (SCB).

Treatment	ADD Non-Carcinogenic (mg·kg ⁻¹ ·Day)	ADD Carcinogenic (mg·kg ⁻¹ ·Day)	HI	CR
S	1.01E+08	8.68E+06	0.06	9.63E-07
SN	5.69E+07	4.88E+06	0.03	5.43E-07
SC	9.93E+07	8.51E+06	0.06	9.48E-07
SCB	8.94E+07	7.66E+06	0.05	8.48E-07

ADD: Average Daily Dose; HI: Hazard index; CR: Carcinogenic risk.

3.3. Effects on Soil Properties

3.3.1. pH and Electrical Conductivity

The soil amended with the two organic treatments, SC (soil+compost) and SCB (soil+compost+biochar), revealed significantly lower pH values than the control soil (S) and the soil amended with the inorganic treatment SN (Soil + nZVI nanoparticles) (Figure 2). This decrease is due to the addition of compost, slightly more acidic than the soil, which alters the redox state of the soil to less oxidising conditions and consequently leads to acidification of the soil by means of the labile organic matter mineralisation [52,53]. Although biochar presents a higher pH than the soil, its addition did not affect this parameter because of the simultaneous application of a higher dose of compost (Table 1). In turn, the nZVI suspension did not increase the soil pH despite its alkaline pH, as reported in previous works [31,37,39,40]. In this context, the optimum pH ranges for plant production varies between 6 and 8. Thus, the applied organic treatments maintained pH in that range whereas nZVI-treated soil slightly exceeded the upper limit. A soil pH higher than 8.0 is considered strongly alkaline for most crops according to Sánchez et al. [54].

As regards EC, only the SCB treatment provoked a significant decrease with respect to the control soil (Figure 1B). This decrease is not worrying since no treatments yielded values above the EC standards established as critical [55].

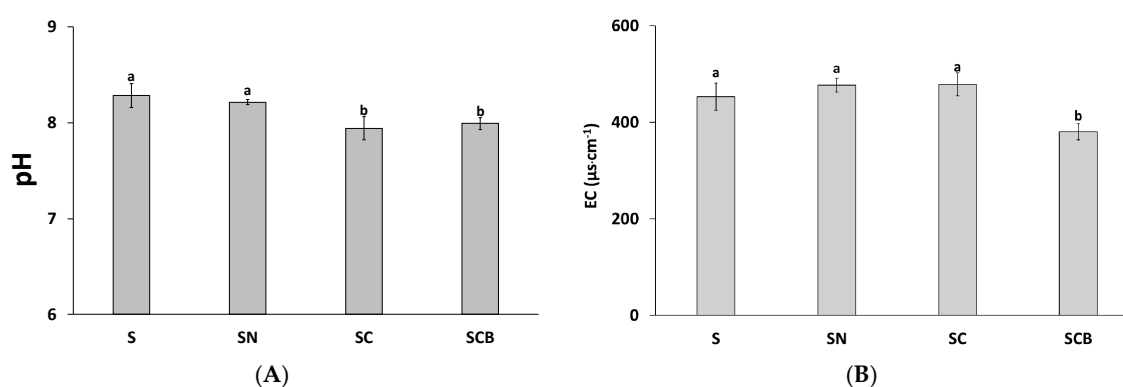


Figure 2. pH (A) and EC (B) variation in polluted soil (S) and in treated soils with nZVI (SN), compost (SC) and compost-biochar (SCB). For each column, different letters in different samples indicate significant differences ($n = 3$, ANOVA; $P < 0.05$).

3.3.2. Organic Matter and Nutrients

The two organic treatments SC and SCB resulted in higher organic matter content than the inorganic treatment SN and the polluted soils (S) (Table 4). The increase in organic matter caused by compost and biochar addition is essential since various soil processes such as biogeochemical cycles, the formation of soil aggregates, nutrient solubilisation, and basic soil properties as cation exchange [56], are highly influenced by the dynamic nature of the organic components. The increase in organic matter caused by SC treatment is due to compost [57–59] while for SCB the increase was due to the mixture of compost and biochar. Authors such as Biederman and Harpole [60] and Madiba et al. [61] showed that biochar causes an increase in carbon in the soil. In fact, biochar as seen in Table 2 had a much higher organic matter content than the compost. However, the difference in OM increase between the SC and SCB treatment was not significant because the biochar was applied in a low dose. On the other hand, the application of the SN treatment did not provide additional OM since it was an inorganic treatment, but neither implied any significant reduction of organic matter in the soil given the low proportion of NPs used.

Concerning to nutrients, at the end of the experimental time, the three amendments applied did not cause significant changes in the K and Na content in the soil. On the contrary, Ca, Mg, and P concentrations increased with the application of the organic amendments (SC, SCB) (Table 4) due to the high amount of nutrients present in the compost (Table 2); similar results were obtained by authors such as Agegnehu et al. [62], Alvarenga et al. [63] and Wang et al. [64]. Furthermore, biochar also has a high nutrient retention capacity and increases carbon storage in the soil [60,61]. Therefore, it can generate better results than other organic amendments when applied together with compost [65], more especially for the long term.

Table 4. Organic matter (OM) and nutrients in polluted soil (S) and in treated soil with nZVI (SN), compost (SC) and compost-biochar (SCB).

		S	SN	SC	SCB
OM		3.0 ± 0.5b	2.5 ± 0.6b	6.8 ± 0.1a	7.4 ± 0.4a
Ca		2645 ± 169b	3022 ± 128b	3735 ± 126a	3833 ± 206a
K	mg·kg ⁻¹	305 ± 32a	298 ± 11a	284 ± 37a	334 ± 15a
Na		50 ± 6a	64 ± 10a	63 ± 5a	52 ± 8a
Mg		1033 ± 12ab	980 ± 8b	1182 ± 74a	1212 ± 58a
P		4.8 ± 0.8b	4.2 ± 0.8b	12.4 ± 0.8a	9.7 ± 3.6a

For each row, different letters in different samples mean significant differences ($n = 3$, ANOVA; $p < 0.05$). Typical deviation is represented by \pm .

3.3.3. Cation Exchange Capacity

The most remarkable result was that samples with both organic treatments (SC and SCB) presented a cation exchange capacity (CEC) significantly higher than in the control soil and in the soil treated with the inorganic amendment (SN) (Table 5). In any case, the cation exchange capacity (CEC) in all the experiments exceeded the recommended values [55], due to the high content of calcite and dolomite of the bulk soil (see Section 3.1). Furthermore, SC and SCB also presented significantly higher Ca²⁺ contents compared to the others. However, no significant differences were found in K⁺, Na⁺, Mg²⁺ and Al³⁺ contents between soils before and after the applied treatments (Table 5). However, the increase in CEC by compost addition did not imply an increase in pH values as previously commented, which contradicts the results obtained by authors such as Forján et al. [66] or Wild [67]. In fact, in our case, a significantly negative correlation was obtained between CEC and pH (-0.79 , $p < 0.01$).

Regarding the nZVI application, despite what might be expected due to the contribution of Fe, no variation in the CEC was observed. This effect agrees with what is proposed by Hazelton and

Murphy [55] who suggested that cations such as manganese (Mn^{2+}), iron (Fe^{2+}), copper (Cu^{2+}) and zinc (Zn^{2+}) are usually present in amounts that do not contribute significantly to the cation complement. Finally, base saturation (V) and aluminium saturation (Al %) did not show significant differences at the end of the experimental time (Table 5).

Table 5. Effective cation exchange capacity, base saturation (V) and aluminium saturation (Al %) in the polluted soil (S) and in the treated soil with nZVI (SN), compost (SC) and compost-biochar (SCB).

		S	SN	SC	SCB
Ca^{2+}		44.10 ± 2.82b	50.37 ± 2.14b	62.25 ± 2.11a	62.52 ± 2.84a
K^{+}		2.60 ± 0.27a	2.54 ± 0.09a	2.42 ± 0.31a	2.86 ± 0.13a
Na^{+}	cmol ₍₊₎ kg ⁻¹	0.73 ± 0.08a	0.93 ± 0.14a	0.91 ± 0.06a	0.75 ± 0.11a
Mg^{2+}		28.71 ± 3.28a	27.23 ± 0.22a	32.84 ± 2.05a	33.33 ± 1.61a
Al^{3+}		0.03 ± 0.00a	0.04 ± 0.00a	0.03 ± 0.01a	0.03 ± 0.00a
CEC		76.1 ± 5.87b	81.1 ± 2.24b	98.4 ± 4.43a	98.2 ± 5.71a
V	%	99.96 ± 0.00a	99.95 ± 0.00a	99.97 ± 0.01a	99.96 ± 0.01a
Al%		0.04 ± 0.00a	0.04 ± 0.00a	0.03 ± 0.014a	0.03 ± 0.00a

For each row, different letters in different samples mean significant differences ($n = 3$, ANOVA; $p < 0.05$). Typical deviation is represented by ±.

3.4. Effects on Plants Growth and As Phytoextraction

Once the pots were dismantled, it was not possible to determine roots biomass. However, it was observed that the abundance of the roots was higher in the organic amendments treated soils, which improves the soil structure, as it is shown in Figure 3.

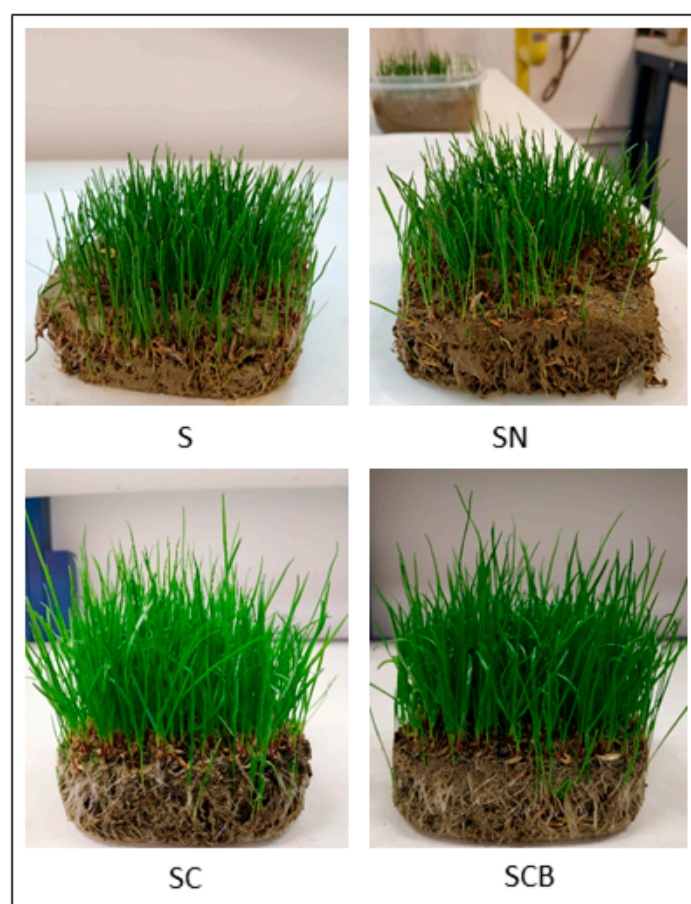


Figure 3. Pots appearance at the end of the experiment.

Several authors have shown that *Lolium perenne* L. can accumulate and tolerate metal(loid)s without its growth being affected by high concentrations [68,69]. As expected, the *Lolium perenne* L. cultivated in the soils treated with organic amendments (SC and SCB) presented a significantly higher fresh biomass than those cultivated in the polluted soil (52–60% increase). In contrast, the inorganic treatment (nZVI) impacted negatively, revealing a decrease of 56% (Table 6). However, the biomass of *Lolium perenne* L. harvested in SN displayed lower As contents than in S (66% decrease), and conversely, the organic amendments facilitated As extraction by the plants resulting in a 60% increase approximately (Table 6).

Table 6. Fresh biomass, nutrients, and metal(loid)s concentration in the plants cultivated in the polluted soil (S) and soils treated with nZVI (SN), compost (SC), and compost-biochar (SCB).

		S	SN	SC	SCB
Fresh biomass		2.5 ± 0.1b	1.1 ± 0.2c	6.3 ± 1.4a	5.2 ± 0.3a
Dry biomass	g	0.43 ± 0.14b	0.17 ± 0.04c	0.86 ± 0.20a	0.73 ± 0.07a
As		0.41 ± 0.03b	0.14 ± 0.02c	1.06 ± 0.17a	0.96 ± 0.02a
Na		52 ± 5d	145 ± 6c	322 ± 11a	207 ± 4b
Mg	mg·kg ⁻¹	1962 ± 86c	947 ± 168d	3874 ± 109a	3279 ± 21b
P		1554 ± 44c	611 ± 4d	4408 ± 130a	3542 ± 118b
K		16,000 ± 452c	7318 ± 200d	45,320 ± 252a	37,195 ± 123b
Ca		3540 ± 150c	1494 ± 230d	7375 ± 240a	6303 ± 81b
Fe		193 ± 5b	126 ± 55b	320 ± 11a	266a ± 36b

For each row, different letters in different samples mean significant differences ($n = 3$, ANOVA; $p < 0.05$). Typical deviation is represented by \pm .

Although as indicated above, the available As concentration determined from RBA extraction was not affected by the organic amendments (see Figure 1), As was mobilised, as it is shown, by the increase of As concentration in the plants (Table 6). In fact, the compost can release dissolved organic carbon and phosphorus, which mobilise As in the soil [27,70–72]. In the case here studied, an increase was detected, and a significant positive correlation was obtained between As concentration in plants and total carbon content (0.61 , $p < 0.05$). As regards biochar, its application mobilises As in soil [73], due to the increase in both dissolved organic carbon and availability of phosphorus, which competes with As for the binding sites [13,74]. Furthermore, the biochar has a large specific surface area with negatively charged functional groups which repel As in anionic forms [75–77]. In addition, it is to be noted that the biochar applied had higher available phosphorus concentration than the polluted soil (Table 2); thus, its application probably caused a release of the retained As, thereby supporting phytoextraction [78]. On the other hand, with the nZVI application, As translocation to the plants decreased due to the As immobilisation in the soil, as described above [31,37,39,40].

Based on the dry biomass, the As concentration in plants and the geometry of the pots (squared, 10×10 cm), it was possible to estimate the amount of As harvested by plants extraction per ha (Figure 4). Considering ecotoxicity, the quantity of As recovered would be higher in the soils treated with organic amendments than in the polluted soil, whereas the amount would be clearly lowered by the nZVI application (around a 65%).

Although As concentration in the plants of both treatments with organic amendments were similar, differences were found in nutrient content in the biomass. In fact, in the studied case, the compost addition produced a significant increase in nutrient concentration than the compost-biochar addition (Table 6), although it is known that biochar may reduce the nutrients availability, allowing plants to use nutrients more efficiently and improving their structure a long time [79]. In this sense, we hypothesise that during the experimental time biochar retained the nutrients in such a way that their release was not done, or at least not entirely. The addition of compost and biochar in soils has benefits in terms

of raising the phytoavailable concentration of K, Mg, Na and P [79] as it was detected in this work. Nutrient input by the compost and retention capacity by the biochar are an adequate combination for plant growth [80,81].

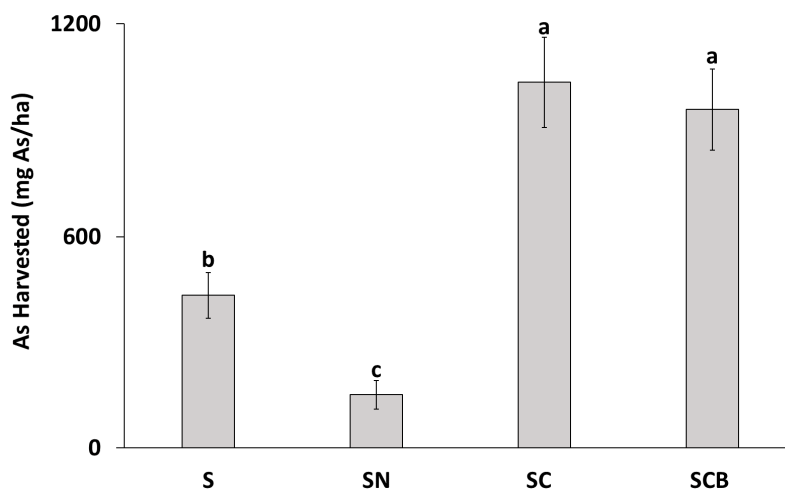


Figure 4. Amount of arsenic harvested by plants extraction per ha in the polluted soil (S), and the treated soils with nZVI (SN), compost (SC) and compost-biochar (SCB). For each column, different letters in different samples indicate significant differences ($n = 3$, ANOVA; $P < 0.05$).

On the other hand, the nZVI application revealed the opposite effect, i.e., a general limitation of nutrient extraction by the plants (Table 6). The addition of iron-rich amendments to soils usually decreases the availability of nutrients, which may imply a decrease of the fresh biomass [51,82,83]. In the present study, although nutrient availability in the soil was not severely lowered, the effects on nutrients extraction by the plants and fresh biomass amount were detected. In the case of Na, it is originated from the commercial nZVI as a by-product of their synthesis, and it was also found to be phytoextracted using barley plants in nZVI-treated soils [39]. As to toxicity, negative effects on phytotoxicity have been reported after addition of excessive doses of iron-based nanoparticles to the soil [37]. Several works have observed that the oxidation of nZVI causes a deficiency of O_2 and an excess of strong reductive Fe(II) in the soil, which in turn impact negatively on plants [84,85]. Phosphorus immobilisation by the nZVI can also affect plants [31]. However, in this work Fe concentration in plants did not increase; thus, the impact on toxicity was only due to a decrease of phosphorus and other nutrients (Table 6).

4. Conclusions

Organic amendments (compost and biochar) and nZVI were tested for remediation of an As-polluted technosol from an urban area. The nZVI application proved to be a useful strategy for immobilising As, resulting in a reduction in both human health risks, and plant ability for As extraction. However, this was also accompanied by a reduction in plant ability for extraction of nutrients such as P, K, Ca, and Mg, thereby impacting negatively plant growth. On the other hand, the organic amendments were useful for plant development due to nutrient addition, although As was also mobilised and extracted by the plants. Furthermore, human health risk was not reduced after compost or compost plus biochar addition. Overall, after comparing opposite strategies of immobilisation and mobilisation, our results concluded that a combination of compost and nZVI could be a good strategy to improve soil properties and plant growth while allowing for low levels of As mobilisation.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4395/10/6/759/s1>, Table S1: XRF Analysis of the marl sample. ($n = 2$). Table S2: Arsenic contents in soil grain size fractions after wet-sieving. Table S3: Minerals phases identified using XRD analysis.

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