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Manganese concentrations in drinking water from villages near banana plantations with aerial mancozeb spraying in Costa Rica: Results from the Infants' Environmental Health Study (ISA)☆

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ABSTRACT

Elevated manganese (Mn) in drinking water has been reported worldwide. While, naturally occurring Mn in groundwater is generally the major source, anthropogenic contamination by Mn-containing fungicides such as mancozeb may also occur. The main objective of this study was to examine factors associated with Mn and ethylenethiourea (ETU), a degradation product of mancozeb, in drinking water samples from villages situated near banana plantations with aerial spraying of mancozeb. Drinking water samples (n = 126) were obtained from 124 homes of women participating in the Infants' Environmental Health Study (ISA, for its acronym in Spanish), living nearby large-scale banana plantations. Concentrations of Mn, iron (Fe), arsenic (As), lead (Pb), cadmium (Cd) and ethylenethiourea (ETU), a degradation product of mancozeb, were measured in water samples. Only six percent of samples had detectable ETU concentrations (limit of detection (LOD) = 0.15 μg/L), whereas 94% of the samples had detectable Mn (LOD = 0.05 μg/L). Mn concentrations were higher than 100 and 500 μg/L in 22% and 7% of the samples, respectively. Mn was highest in samples from private and banana farm wells. Distance from a banana plantation was inversely associated with Mn concentrations, with a 61.5% decrease (95% CI: −97.0, −26.0) in Mn concentrations for each km increase in distance. Mn concentrations in water transported with trucks from one village to another were almost 1000 times higher than Mn in water obtained from taps in houses supplied by the same well but not transported, indicating environmental Mn contamination. Elevated Mn in drinking water may be partly explained by aerial spraying of mancozeb; however, naturally occurring Mn in groundwater, and intensive agriculture may also contribute. Drinking water risk assessment for mancozeb should consider Mn as a health hazard. The findings of this study evidence the need for health-based World Health Organization (WHO) guidelines on Mn in drinking water.

1. Introduction

Several studies have shown a negative association between elevated manganese (Mn) in drinking water and children's neurodevelopment, behavior, and academic achievement (Bouchard et al., 2011; He et al., 1994; Khan et al., 2014, 2012; Oulhote et al., 2014; Wasserman et al., 2005; Woolf et al., 2002; Zhang et al.,

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1995), whereas studies on the effects of elevated Mn on fetal growth have shown inconsistent findings (Chen et al., 2014; Eum et al., 2014; Mora et al., 2015; Takser et al., 2004; Yu et al., 2013; Zota et al., 2009). Mn is an essential element found in the earth's crust. Water percolating through soil and rock can dissolve minerals containing Mn, often concurrent with iron (Fe) (Homoncik et al., 2010). In aquifers where dissolved oxygen and redox potential are low, higher levels of Mn can be found in the dissolved reduced state (Mn(II)) (Thomas et al., 1994). The highest concentrations of Mn are found in groundwater, whereas surface water rarely presents high concentrations (Thomas et al., 1994).

Elevated Mn concentrations in drinking water that surpass health-based value of 0.4 mg/L (WHO, 2011) have been reported in studies from around the world (Frisbie et al., 2012; Phan et al., 2013). While in most of these studies elevated Mn in groundwater due to bedrock was identified as the source of contamination, in some cases Mn contamination was due to industrial activities, such as mining and dump sites (Frisbie et al., 2012). Agricultural applications of dithiocarbamate fungicides that contain approximately 20% Mn and are commonly used worldwide, such as mancozeb (FAO (Food and Agriculture Organization of the United Nations), 1980), also have been identified as a possible source of environmental Mn contamination (Gunier et al., 2013; Mora et al., 2014).

Investigations on the environmental fate and risk evaluations of mancozeb have focused almost exclusively on its degradation product ethylenethiourea (ETU), considered more toxic to humans than mancozeb (U.S. EPA (U.S. Environmental Protection Agency), 2005a,b). In soil and agricultural waters, ETU is rather rapidly degraded to ethylene urea; its half-life is 1–7 days under field conditions (Cruickshank and Jarrow, 1973; Ross and Crosby, 1973; Xu, 2000). Sediments of drain channels in banana plantations with mancozeb spraying have shown low ETU and elevated Mn levels (Melgar et al., 2008). A study performed near banana plantations sprayed with mancozeb for 10 years, showed elevated Mn and low ETU levels in soil, but elevated ETU and low Mn levels in surface and sub-surface waters (Geissen et al., 2010).

In Costa Rica, the Infants' Environmental Health Study (ISA, for its acronym in Spanish), a community-based birth cohort study, is examining maternal exposure to pesticides used in banana plantations and the effects on children's growth and neurodevelopment (Mora et al., 2015, 2014; van Wendel de Joode et al., 2014). Pregnant women recruited into the ISA study lived within five km of banana plantations that are aerially sprayed with mancozeb on a weekly basis (Barraza et al., 2011; Ramirez, 2010). Urinary ETU concentrations, traditional biomarker used to assess mancozeb exposure, were elevated among these women and inversely associated with residential distance from a banana plantation, washing agricultural work clothes, and working in agriculture during pregnancy (van Wendel de Joode et al., 2014). Notably, there was no relation between urinary ETU levels and self-reported drinking water consumption from wells (van Wendel de Joode et al., 2014). Blood and hair Mn were likewise elevated among these pregnant women (Mora et al., 2014). Hair Mn levels were inversely associated with residential distance from a banana plantation, but positively associated with working in agriculture prior to pregnancy and Mn concentrations in drinking water (Mora et al., 2014), indicating that drinking water is a potential source of Mn in this population. These findings suggest that both urinary ETU and blood and hair Mn concentrations are partially due to exposure from aerial spraying of mancozeb.

The objectives of this study were: (*i*) to measure Mn, ETU and the metals arsenic (As), cadmium (Cd), iron (Fe) and lead (Pb) as well as the physic-chemical properties of drinking water in villages located within 5 km of banana plantations that aerial spray with mancozeb; (*ii*) to examine the associations between concentration of these elements in the drinking water and water supply system, distance between source of water supply and banana plantations, distribution system, date and time of sampling; (*iii*) to explore the relation between metal concentration and socio-demographic factors. As, Cd, and Pb were measured because of being neurotoxic and Fe was determined because it is often concurrent with Mn in natural environments.

2. Methods

2.1. Measurement strategy and sampling

Between May and October 2011, a drinking water sample was collected in the homes of 124 (28%) ISA study participants who had a study visit already scheduled during this period to collect urine, blood, and hair samples and administer an interview to the women to obtain information on women's sociodemographic characteristics, medical and occupational history, partners' occupation, pesticide use at work and at home, lifestyle habits, quality and type of housing, basic dietary information (including frequency of fruit and vegetable intake), and source of drinking water (Van Wendel de Joode et al., 2014; Mora et al., 2014). In two homes, drinking water came from two separate sources; therefore, in each of these two homes two drinking samples were obtained, making a total of 126 samples. Samples were collected in May ($n = 58$, 46%), June ($n = 31$, 24%), July and August ($n = 16$, 13%), and September and October ($n = 21$, 17%) 2011, between 8:00 and 19:00. To explore concordance of ETU, Mn and other metal concentrations, and physical-chemical characteristics over time, a second sample was collected in 30 of the 124 homes, between August and October 2011 [mean time after the first sample ± standard deviation (SD) = 14.3 weeks ± 3.6; range = 6.9–20.9]. Pregnant women for whom a drinking water sample was collected ($n = 124$) had similar age (mean ± SD = 24 years ± 6.7), education (7 years ± 3.0), and country of birth (15% were immigrants) characteristics, and similar residential distance from banana plantations [mean ± SD = 479 m (m) ± 678] compared to all of the 451 women enrolled in the ISA study who were on average 24 years old (SD = 6.8), had seven years of education (SD = 2.8), 19% were immigrants, lived at a mean distance of 453 m (SD = 657) from banana plantations.

Water collection procedures have been described elsewhere (Mora et al., 2014). Briefly, in houses with piped-in water ($n = 95$), tap water samples of 10 mL were collected in polypropylene tubes (PerformR Centrifuge tubes, Labcon, Petaluma, CA) using the following standardized procedure (adapted from van der Hoven and Slaats, 2006): open the tap for one minute, reduce flow, and collect sample. In houses with no piped water supply ($n = 31$), drinking water was collected from wells, community taps, rivers, or bottled water and stored in large plastic containers. Water samples of 10 mL were collected directly from the plastic containers.

For logistical reasons, physicochemical parameters such as pH, electrical conductivity, and temperature were measured in 83 (66%), 79 (63%), and 82 (65%), respectively, out of the 126 water samples. A pH electrode (HI 1270 screw-type pH-electrode) was used to measure pH, and a conductivity and temperature tester (HI 73311 EC/TDS; HANNA Instruments) was used to measure electrical conductivity and temperature. The instruments were calibrated daily according to the procedures indicated by the manufacturers.

2.2. Study site

Water samples were obtained in 56 neighborhoods from 40 villages. Fig. 1 illustrates the banana farm areas and location of all of the drinking water samples sites, the banana farm areas,

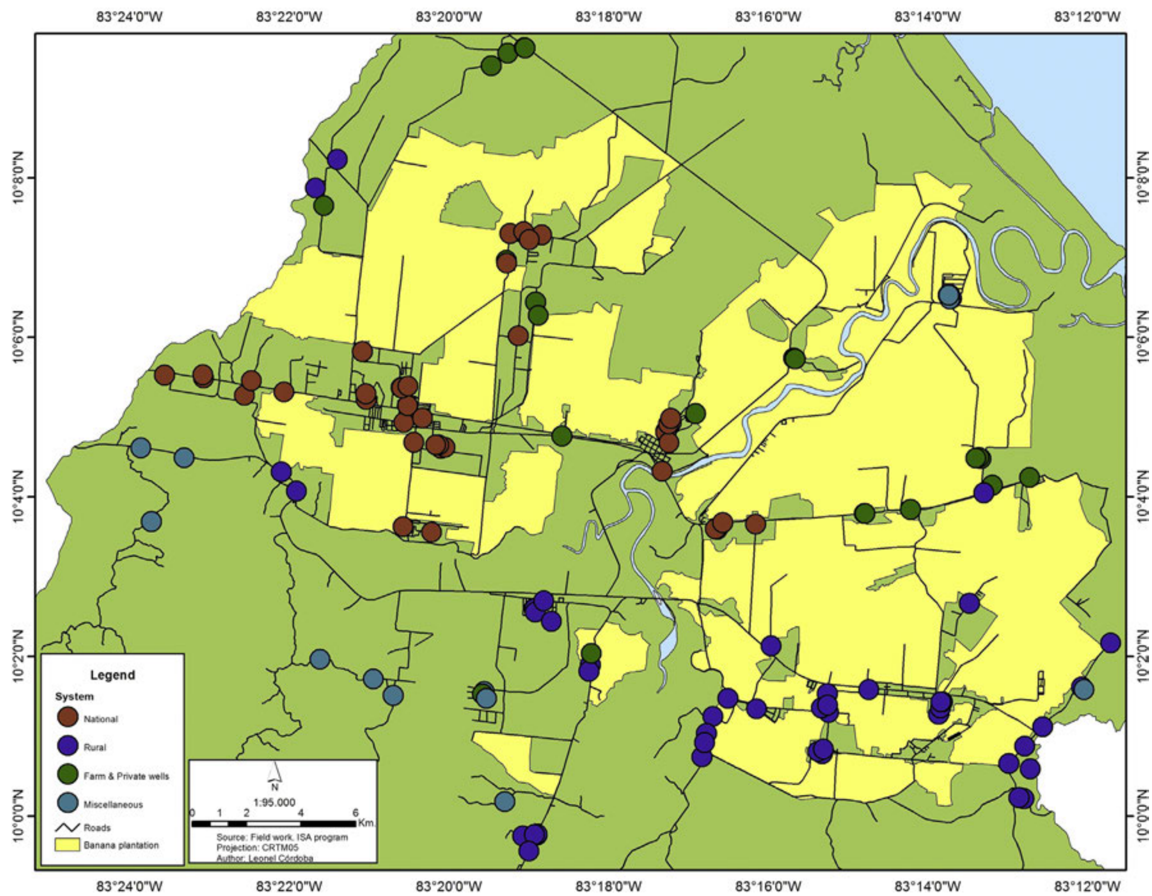

Fig. 1. Map with banana farms (dark grey [yellow in web version]) and homes in which drinking water was sampled according to four water supply systems as indicated in legend.

categorized based on type of water supply system: national, rural, banana farm and private wells (grouped together), and miscellaneous drinking water sources. Supplementary Fig. S—1 illustrates a banana farm well and Supplementary Fig. S-2a-e show some of the private wells that supplied drinking water.

The distribution of the 126 water samples with respect to water supply system and other characteristics are presented in Table 1. The National Costa Rican Water and Sanitation Institute (AyA, for its acronym in Spanish, referred to henceforth as national supply system) supplied 22 neighborhoods [42 samples (33.5%)] with three different supply systems. One took its water from a mixture of sources, including two wells (10 and 30 m in depth) and two springs, while the other two were from single wells (30 m and 60 m). Drinking water from the national supply system was chlorinated. Nine Administrative Associations of Rural Water and Sanitation Systems (ASADAS, for its acronym in Spanish, referred to henceforth as rural supply systems) supplied 16 neighborhoods (46 samples = 36.5%) and collected their water from five wells and four springs or streams. Three of the wells were approximately 75 m in depth, while the depth of the other two was unknown. The water was chlorinated and one of the rural providers that took their water from a well of unknown depth reported having a chemical treatment system for Mn.

Banana farm companies supplied drinking water in three of the

Table 1
Distribution of drinking water samples (n = 126) with respect to characteristics of water supply systems.[a]

Type of water supply system (n, % of samples)	Neighborhoods[a] (n)	Number of systems (N) and type of sources[b] (number of samples)	% Piped-in	Mean ± SD distance to banana plantation (km)
National (n = 42, 33%)	22	N = 3: One mixed system (n = 21), two deep wells (n = 21)	83	0.17 ± 0.13
Rural (n = 46, 37%)	16	N = 5: Three deep wells (n = 20), two wells of unknown depth (n = 10), four surface water (n = 16)	100	1.91 ± 1.86
Banana farm wells (n = 5, 4%)	3	N = 3: All shallow wells (n = 5)	100	0.01 ± 0.00
Private wells (n = 18, 14%)	13	N = 11: All shallow wells (n = 18)	6	0.61 ± 0.85
Miscellaneous (n = 15, 12%)	10	N = 5: Rain water (n = 1), three streams (n = 9), transported water (n = 5)	53	1.90 ± 1.90
Total (n = 126, 100%)	64	N = 31 (n = 126)	75	1.07 ± 1.56

Abbreviations: N/A = not applicable.
[a] Eight neighborhoods had more than one supply system.
[b] Deep wells were 30–75 m deep; mixed source was water obtained from two wells that were 10 and 30 m and from a spring; surface water was obtained from springs and streams; shallow wells were 3–10 m deep; transported water was obtained from a deep well (30 m) of one of the national systems and was transported in tanks to a village located at less than 50 m from banana plantations; rain water was obtained by collecting water from a roof.

56 neighborhoods that were sampled. In these neighborhoods, banana companies had their own wells and provided drinking water to workers' homes and, in some instances, the surrounding community (Table 1 and Fig. S-1). Private wells (11 wells, 13 samples) were generally dug wells of three to ten meters deep. The maintenance of the private wells varied, but was generally very poor. Some of the wells were simply holes dug in the ground, while others had concrete walls, sometimes surrounded by a plate of concrete (a-e). Six wells (33.3%) did not have a cover. Finally, three miscellaneous delivery systems included: rainwater (one sample), water from untreated streams (six streams, nine samples) and tanks that contained water transported from one of the national systems to a village without access to drinking water (five samples). Of the 126 drinking water samples, 95 samples (75%) were obtained directly from piped-in taps in homes, 16 (13%) were obtained from outdoor wells used for drinking water, and 15 (12%) from containers filled with water that the families drank (Table 1).

2.3. Analyses for Mn, Fe, As, Pb, Cd, and ETU

Drinking water samples were stored at −20 °C until their shipment to Lund University Hospital, Sweden. Water Mn, Fe, As, Pb, and Cd concentrations were measured in acidified samples (2% HNO_3) using inductively coupled plasma mass spectrometry (Thermo X7, Thermo Elemental, Winsford, UK). Analytical accuracy was estimated based on reference materials (SLRS-2, Riverine Water Reference Material for Trace Metals, Ottawa, CA). The results (mean ± SD) for reference material versus (vs) certified sample (n = 14) were: 8.9 ± 0.3 μg/L vs 10.1 ± 0.3 μg/L for Mn, 134 ± 4.5 μg/L vs 129 ± 7.0 μg/L for Fe, 0.90 ± 0.03 μg/L vs 0.77 ± 0.09 μg/L for As, 0.037 ± 0.004 μg/L vs 0.028 ± 0.004 μg/L for Cd, and 0.129 ± 0.011 μg/L vs 0.129 ± 0.011 μg/L for Pb. All samples were analyzed in duplicate and the method imprecision (calculated as the coefficient of variation for duplicate measurements) was 2.5% for Mn, 2.8% for Fe, 2.1% for As, 15% for Cd, and 6.1% for Pb. The analytical limit of detection (LOD), defined as three times the SD of the blank samples, was estimated at 0.05 μg/L for Mn, 10 μg/L for Fe, 0.06 μg/L for As, 0.02 μg/L for Cd, and 0.05 μg/L for Pb.

ETU concentrations in water were analyzed according to (Ekman et al., 2013) with the minor modification of omitted hydrolysis. Briefly, water was added with isotopically labeled ETU and aliquots of 20 μL were analyzed using liquid chromatography triple quadrupole mass spectrometry. The LOD was 0.15 μg ETU/L. All samples were prepared in duplicates, worked-up and analyzed on different days.

2.4. Information on water sources

For the major water distributers, the national and rural supply systems, information on location of water source, type of water source (well, spring, stream), well depth, and water treatment was obtained by interviewing the administrators of the water distribution systems. For wells administered by the banana farms, private wells, and miscellaneous sources (stream, spring, and rain water) information was obtained by direct observations and from the study participants. Except for one of the rural supply systems, no treatment technologies are being used to remove Fe or Mn from the water.

All drinking water sources were located on a geocoded map of the Matina County using ArcGIS 10.0 software (Esri, Redlands, CA) and aerial photos from the Costa Rica Airborne Research and Technology Applications (CARTA) 2005 mission. Participants' houses and banana plantations were geolocated using a Global Positioning System (GPS) receiver (Garmin etrex Venture HC, Olathe, KS). Plantation locations were measured as static areas of at least four points when possible. Proximity of the water source to banana plantations was estimated using CARTA 2005 mission photos and GPS coordinates. Euclidean distances were measured from the point representing the water source to the closest plantation.

2.5. Statistical analyses

No statistical analyses were performed for ETU and Cd, because ≤6% of samples had concentrations above LOD of, respectively, 0.15 and 0.05 μg/L. Descriptive statistics were used to characterize Mn, Fe, As, and Pb concentrations, as well as the physicochemical characteristics of the drinking water samples (pH, temperature, and conductivity). For Mn, Fe, As and Pb, samples below LOD were set at half the square root of the LOD (Lubin et al., 2004).

Since the concentrations of Mn, Fe, As, and Pb were strongly skewed, non-parametric tests were used and metal concentrations were ln-transformed to normalize residuals when using parametric tests. Water pH, temperature, and conductivity followed normal distributions.

To discover relations among Mn, Fe, As, and Pb, pH, temperature, and conductivity, general linear Principal Component Analysis (PCA) was used after standardizing the values of each variable into z-scores. Principal components (PC) with eigenvalue greater than one, subjected to a varimax orthogonal rotation, were retained. To analyze concordance between the repeated samples (n = 60 from 30 homes) Spearman's correlation coefficients and two-sample paired T-test were used. Subsequently, Wilcoxon/Kruskal-Wallis test (Rank Sums) was used to look at differences in medians across categories of the water supply systems (national, rural, banana and private wells, miscellaneous). In addition, to identify factors that may explain metal concentrations and physical-chemical characteristics separate linear regression models were fitted with ln-Mn, ln-Fe, ln-As, ln-Pb, pH, temperature and conductivity as dependent variables, and water supply system (national, rural, banana and private wells, miscellaneous), distance from source of water supply to banana plantations (kilometers), distribution system (piped-in or not), date of sampling, time of sampling (morning, afternoon) as independent variables. Independent variables with $p < 0.10$ in one of the bivariate models were retained in the multivariate models. For metals, % change in concentrations was calculated for a one-unit increase in the independent variable while all other variables in the model are held constant was calculated as 100*(beta coefficient). Residuals of the regression models were tested for normality (Shapiro-Wilk test) and outliers.

Since drinking water samples were collected from a large number of neighborhoods (n = 56) with different water delivery systems, covering a wide geographic area, with different geologic conditions, Decision Tree method of recursive partition modeling was used to explore the clustering of ln-Mn with respect to neighborhood (Cook and Goldman, 1984). The output is a tree diagram, with the split maximizing the difference in responses between the two branches of the split. Splitting was limited to three passes in order to ensure adequate numbers (n ≥ 19) in each cluster. Information was provided on the median and interquartile range (IQR) within each cluster, as well as the model's R^2 and the corrected Akaike's Information Criterion (AIC). Subsequently, the clusters were stratified by water supply system (national, rural, banana and private wells, miscellaneous) and distance from a banana plantation (<50 m, ≥50 m) as results from the multivariate models showed these factors predicted Mn water concentrations.

Finally, socio-demographic characteristics (age, education, income, immigrant) of participants living in the neighborhood groupings identified by Decision Tree method of recursive partition modeling were associated with metal concentrations in drinking water by comparing median concentrations between groups with Wilcoxon/Kruskal-Wallis test (Rank Sums).

Effects were considered statistically significant with $p < 0.05$ based on two-tailed tests. All analyses were conducted using JMP 8 (SAS Institute, Cary, NC).

3. Results

3.1. Metals and ETU in drinking water

ETU was detected in eight (6%) out of 126 samples with concentrations ranging from 0.15 to 0.25 μg/L. Cd was detected in only two (2%) out of the 126 samples, with concentrations of 0.09 μg/L and 0.10 μg/L.

Table 2 presents the distributions of metal concentrations that were detected in ≥50% of the 126 water samples, as well as the distributions of pH, conductivity, and temperature. Mn was detected in 119 (94%) water samples. Overall, 33% of drinking water samples had Mn concentrations >50 μg/L, the US-EPA aesthetic recommendation (US EPA, 2010), and 22% surpassed the 100 μg/L aesthetic recommendation by WHO (WHO, 2011). In addition, 9.5% surpassed the WHO health-based value, but not formal guideline, of 400 μg/L (WHO, 2011); and 7% was >500 μg/L, the maximum permissible Mn concentration in drinking water in Costa Rica (LA GACETA, 2005). With respect to the WHO guidelines for other metals (WHO, 2011), only one water sample had As concentrations >10 μg/L, whereas none of the samples had Pb concentrations >10 μg/L. To date, there is no health-based guideline for Fe, but both the US-EPA (US EPA, 2010) and the Costa Rican Water Regulation (LA GACETA, 2005) recommend 300 μg/L as an aesthetic guideline, value that was surpassed by 13.5% of the water samples.

Results of PCA indicated that two PC had eigenvalues >1 and accounted for 61% of the variability (Table S1). Fig. 2 shows that the first PC (PC1) consisted mainly of Mn, Fe, As and conductivity, whereas the PC2 consisted mainly of pH and Pb.

With respect to first and second samples, Mn, Fe, As, and conductivity were highly correlated (Spearman's rho = 0.84–0.93) whereas Pb, pH and temperature were less correlated (Spearman's rho = 0.69, 0.75, 0.52, respectively). Only water As concentrations from the second sampling period were slightly higher compared to those from the first period (mean difference of ln-As = 0.11; 95% CI: 0.00, 0.23; $p = 0.05$). Other variables did not differ between sampling periods.

Table 3 presents the medians and IQRs for metal concentrations and physicochemical parameters. Drinking water samples from the banana farm wells had the highest concentrations of Mn (median = 1152 μg/L; IQR = 196–1365), followed by private wells (median = 293; IQR = 23.7–562; data not shown). There were no statistically significant differences in Mn concentrations between

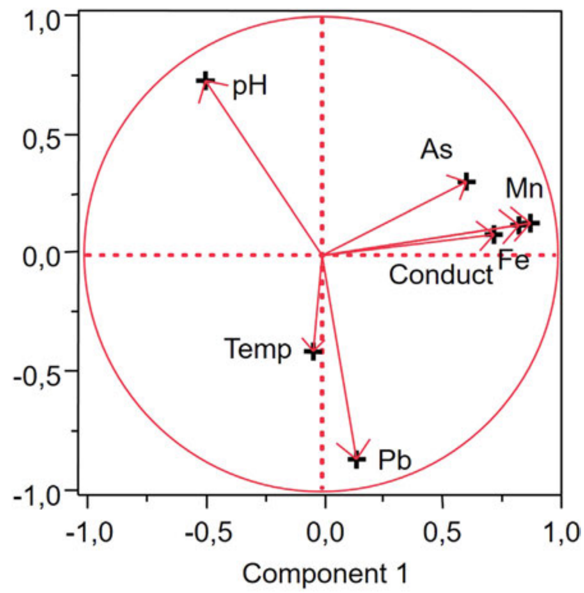

Fig. 2. Loading plot of principal component 1 (x-axis) and 2 (y-axis) indicating eigenvalues of Mn, Fe, As, Pb, pH, conductivity and temperature that were standardized to z-scores prior to analysis (n = 79).

these two types of wells (p = 0.59), so we grouped them for further analyses. More than half (52%) of private and banana farm wells had Mn concentrations ≥300 μg/L compared to only 2% for the other distribution sources. Banana farm and private wells also presented the highest concentrations of Fe and As. Water Pb concentrations were low in all systems, and only one drinking sample, from rainwater, had a Pb concentrations >5 μg/L, probably due to the leaching of lead from the roof covering. The lowest pH and highest conductivity were observed for drinking water from farm and private wells, whereas miscellaneous sources had the lowest temperature and conductivity. Mn concentrations correlated moderately and strongly with Fe and As (Spearman's rho = 0.39–0.82; Table 3), and correlations between Mn and Fe were stronger for banana farms and private wells and miscellaneous systems. Only for rural water systems, Mn concentrations were moderately correlated with temperature. In contrast, Mn concentrations correlated with conductivity in all systems except for the rural one.

Bivariate analyses showed that Mn concentrations in piped-in tap water samples (n = 95, median = 1.5 μg/L, IQR = 0.20–64.5) were lower compared to samples collected directly from wells or storage tanks with water from community systems, rain water, or obtained from other miscellaneous systems (n = 31, median = 61.5 μg/L, IQR = 6.3–417; $p < 0.001$; data not shown). Water samples collected directly from wells and miscellaneous systems also presented significantly higher Fe concentrations (median = 192 μg/L, IQR = 132–347) compared to piped-in water

Table 2
Distribution of manganese, iron, arsenic, lead, pH, conductivity and temperature in drinking water samples (n = 126).

Variable	N	%>LOD	Mean ± SD	Median (P25-P75)	P90	Max
Mn (μg/L)	126	94	123 ± 297	5.4 (0.34–86.8)	399	1600
Fe (μg/L)	126	100	261 ± 503	139 (53.1–197)	487	3105
As (μg/L)	126	98	1.1 ± 1.7	0.59 (0.28–1.2)	3.2	14.1
Pb (μg/L)	126	57	0.20 ± 0.59	0.08 (0.04–0.16)	0.4	6.3
pH	83	N/A	7.6 ± 0.41	7.7 (7.5–7.9)	8.1	8.2
Conductivity (μmhos/cm)	82	N/A	273 ± 116	254 (198–336)	403	630
Temperature (°C)	79	N/A	29.0 ± 1.5	29 (28–30)	31	33

Abbreviations: N/A = not applicable.

Table 3
Median (percentile 25–75) of metal concentrations (Mn, Fe, As, Pb) and physical-chemical (pH, temperature and conductivity) water characteristics, and their correlation (Spearman's rho) with Mn.

Characteristic	National			Rural			Banana farm & private wells			Miscellaneous		
	n	P50 (P25-P75)	ρ	n	P50 (P25-P75)	ρ	n	P50 (P25-P75)	ρ	n	P50 (P25-P75)	p
Mn (μg/L)	42	2.0 (0.2–26.8)		46	1.2 (0.2–89.6)		23	391[a] (30.7–1093)		15	6.7 (1.2–61.5)	
Fe (μg/L)	42	98.6 (46.6–162.4)	0.39*	46	111 (57.9–172)	0.39**	23	347[b] (201–1039)	0.77***	15	79 (52.8–165)	0.82***
As (μg/L)	42	0.67 (0.59–1.19)	0.71***	46	0.41 (0.25–1.0)	0.49***	23	0.88[c] (0.30–2.6)	0.67***	15	0.21 (0.08–0.47)	0.54*
Pb (μg/L)	42	0.08 (0.04–0.20)	−0.05	46	0.08 (0.04–0.21)	−0.25#	23	0.07 (0.04–0.15)	0.12	15	0.04 (0.04–0.08)	0.12
pH	28	7.75 (7.67–7.90)	0.32	30	7.8 (7.6–8.0)	−0.10	18	7.2[d] (6.8–7.6)	0.24	7	8.0 (7.9–8.1)	0.36
Temp (°C)	27	29.5 (28.7–30.2)	0.14	27	28.9 (28.0–29.7)	0.43*	18	28.9 (27.5–29.8)	−0.28	7	28.2[e] (26.3–28.5)	0.04
Conductivity (μmhos/cm)	28	211 (173–352)	0.81***	29	242 (227–285)	−0.01	18	340[f] (269–491)	0.57*	7	178[g] (95–204)	0.88**

#$p < 0.10$ *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$.
[a] Banana farm and private wells have significantly more Mn compared to the others (p < 0.001).
[b] Banana farm and private wells have significantly higher Fe compared to the others (p < 0.001).
[c] Banana farm and private wells have significantly higher As compared to miscellaneous water systems (p < 0.001).
[d] Banana farm and private wells have significantly lower pH (p < 0.001) pH compared to the others.
[e] Miscellaneous sources have lower mean temperature compared to the national system (p = 0.04).
[f] Banana farm and private wells have higher conductivity compared to the others (p < 0.01).
[g] Miscellaneous sources have significantly lower conductivity compared to others ($p < 0.05$).

samples (median = 113 μg/L, IQR = 49.8–172; $p < 0.001$), and lower pH (median = 7.4, IQR = 6.8–8.0; and median = 7.7, IQR = 7.6–7.9, respectively; $p = 0.03$). Other metals and water physicochemical parameters were similar in piped-in and non piped-in systems (data not shown). Drinking water samples from sources that were embedded in banana plantations (<50 m) presented significantly higher concentrations of Mn (n = 19, median = 73.9 μg/L, IQR = 0.70–1152) compared to those located farther away (n = 107, median = 3.3 μg/L, IQR = 0.32–75.0; $p = 0.02$).

Embedded sources presented significantly higher Fe concentrations ($median_{Fe}$ = 221 μg/L), slightly higher As concentrations ($median_{As}$ = 0.63 μg/L), and similar Pb concentrations ($median_{Pb}$ = 0.06 μg/L) compared to non-embedded sources ($median_{Fe}$ = 113 μg/L, $p_{Fe} < 0.001$; $median_{As}$ = 0.55 μg/L, $p_{As} = 0.07$; $median_{Pb}$ = 0.08 μg/L, $p_{Pb} = 0.28$; respectively). In addition, embedded water sources had slightly lower temperatures ($mean_T$ = 28.3 °C) and pH ($mean_{pH}$ = 7.45), but significantly higher conductivity ($mean_C$ = 385 and 252 μmhos/cm, respectively, $p < 0.001$) than non-embedded sources ($mean_T$ = 29.2 °C, $p_T = 0.07$; $mean_{pH}$ = 7.68, $p_{pH} = 0.07$; $mean_C$ = 252 μmhos/cm, $p_C < 0.001$).

Metal concentrations, pH, and conductivity were similar in water samples obtained in May (n = 58) and June to October (n = 68), but temperature was lower in water samples obtained in May ($p = 0.007$). Time of sampling (hours) was inversely associated with ln-Mn (β = 0.19; 95% CI: −0.40, 0.01; $p = 0.06$) and ln-Fe concentrations (β = −0.07; 95% CI: −0.13, 0.00; $p = 0.06$), but not with ln-As or ln-Pb levels.

3.2. Factors explaining metal concentrations and water characteristics

Table 4 presents the results of the multiple regression analyses for metals with distance (in m, continuous variable), water access (piped-in/other), month of sampling (May or June to October), time of sampling (continuous variable), and water distribution system. Distance from a banana plantation was inversely associated with water Mn [% change = −61.5, 95% confidence interval (CI): −97.0, −26.0], Fe (% change = −11.2, 95% CI: −22.3, −0.1) and As concentrations (% change = −29.7, 95% CI: −42.2, −17.2; Table 4). The distribution system predicted Mn and Fe concentrations with significantly higher concentrations for banana farm and private wells compared with the national water supplier (Table 4). Miscellaneous sources also had significantly lower Fe concentration compared with the rest. Distance from a banana plantation was inversely associated with As, and Farm and private wells presented significantly higher As in comparison with the national water systems and miscellaneous sources. For Pb, piped-in drinking water was significantly lower compared to other means of drinking water collection.

The pH, temperature and conductivity decreased with distance from a banana plantation, although temperature did not reach statistical significance. The pH was significantly lower in the non piped-in systems with the lowest values measured in drinking water from private wells (mean = 6.91 °C, 95% CI: 6.73, 7.18). There was a tendency towards lower temperatures for the other water sources, which included systems from streams. Conductivity was higher in the farm and private wells compared to the other water sources.

3.3. Grouping of neighborhoods

Results from recursive partition modeling of ln-transformed Mn concentrations provided clustering of the neighborhoods into four groupings (A-D; $R^2 = 0.85$; AIC: 413). Fig. 3 presents the distribution of Mn in each water delivery system with respect to four neighborhood groupings and stratified by distance from banana plantations (<50 and ≥ 50 m). The lowest Mn concentrations (median = 0.07 μg/L; maximum (max) = 0.16) were measured in water samples from taps furnished by one of the national distribution systems that was supplied by a 30 m deep well situated <50 m from a banana plantation (Fig. 3). The highest Mn concentrations (median = 58.3 μg/L; max = 475) of the three national distribution systems surveyed in this study were measured in water samples originating from a 60 m deep well located at 325 m from banana plantations; nine (56%) of the homes on this system had Mn concentrations ≥ 50 μg/L. For the national providers, there was a decrease in Mn concentrations with respect to time of sampling (Spearman's rho = −0.33; p = 0.03; data not shown). This association was highest in the system with the deepest well (60 m) and the highest Mn (Spearman's rho = −0.71; p = 0.002). In this system, which included 16 different sampling sites, there was almost a three-fold decrease in Mn concentrations when comparing samples taken before noon (median = 116 μg/L) to those taken in the afternoon (median = 29 μg/L) (Supplemental Fig. S–3).

Drinking water originating from rural systems was in all neighborhood groupings (Fig. 3). The rural systems that took their water from streams and springs were located 2.6–6.5 km from

Table 4
Results of multivariate regression analysis with percentage change (95% CI) in Mn, Fe, As and Pb concentrations, and % change (95% CI) in pH, temperature, and conductivity, per one unit increase in the independent variable.

Independent variable	% Change (95% CI)				% Change (95% CI)		
	Mn (n = 126)	Fe (n = 126)	As (n = 126)	Pb (n = 125)[a]	pH (n = 89)	Temperature (°C) (n = 79)	Conductivity (μmhos/cm) (n = 82)
Distance from water source to banana plantations (km)	−61.5*** (−97.0, −26.0)	−11.2* (−22.3, −0.1)	−29.7*** (−42.2, −17.2)	−0.1 (−14.3, 14.1)	−0.07* (−0.13, −0.01)	−0.30* (−0.59, −0.01)	−23* (−43, −4.4)
Time (hours)	−15.8# (−34.2, 2.5)	−4.7 (−10.5, 1.0)	−1.9 (−8.4, 4.5)	2.4 (−5.0, 9.7)	0.01 (−0.02, 0.04)	−0.01 (−0.13, 0.12)	−9.6* (−18, −1,2)
Month of sampling (May)	−10.7 (−60.2, 38.8)	8.7 (−6.8, 24.1)	−12.9 (−30.5, 4.5)	11.1 (−8.7, 30.9)	0.01 (−0.07, 0.08)	−0.41* (−0.78, −0.06)	1.6 (−22.25)
Piped-in	−23.3 (−96.4, 49.7)	1.8 (−21.0, 24.7)	32.1* (6.4, 57.9)	−35.3* (−64.7, −6.3)	0.09# (−0.02, 0.19)	−0.10 (−0.58, 0.38)	36* (5, 67)
Distribution system[b]							
National	−163*** (−252, −74.3)	−52.3*** (−80.2, −24.5)	0.6 (−30.8, 31.9)	16.8 (−18.8, 52.5)	−0.01 (−0.15, 0.13)	0.41 (−0.24, 1,1)	−14 (−56, 27)
Rural	−65.8 (−157, 25.5)	−21.0 (−49.6, 7.6)	17.1 (−15.0, 49.3)	32.5# (−4.0, 69.0)	0.09 (−0.04, 0.23)	0.39 (−0.26, 1.0)	−32 (−74, 10)
Banana farm & private wells	204*** (94.6, 314)	109.8*** (75.4, 144.1)	50.8* (12.1, 89.4)	−24.0 (−67.9, 19.9)	−0.44*** (−0.59, −0.29)	0.02 (−0.67, 0,72)	118*** (72, 163)
Adjusted R^2	0.29	0.37	0.27	0.02	0.39	0.14	0.33

#$p < 0.10$ *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$.
[a] One outlier was excluded from analysis.
[b] Miscellaneous is reference category.

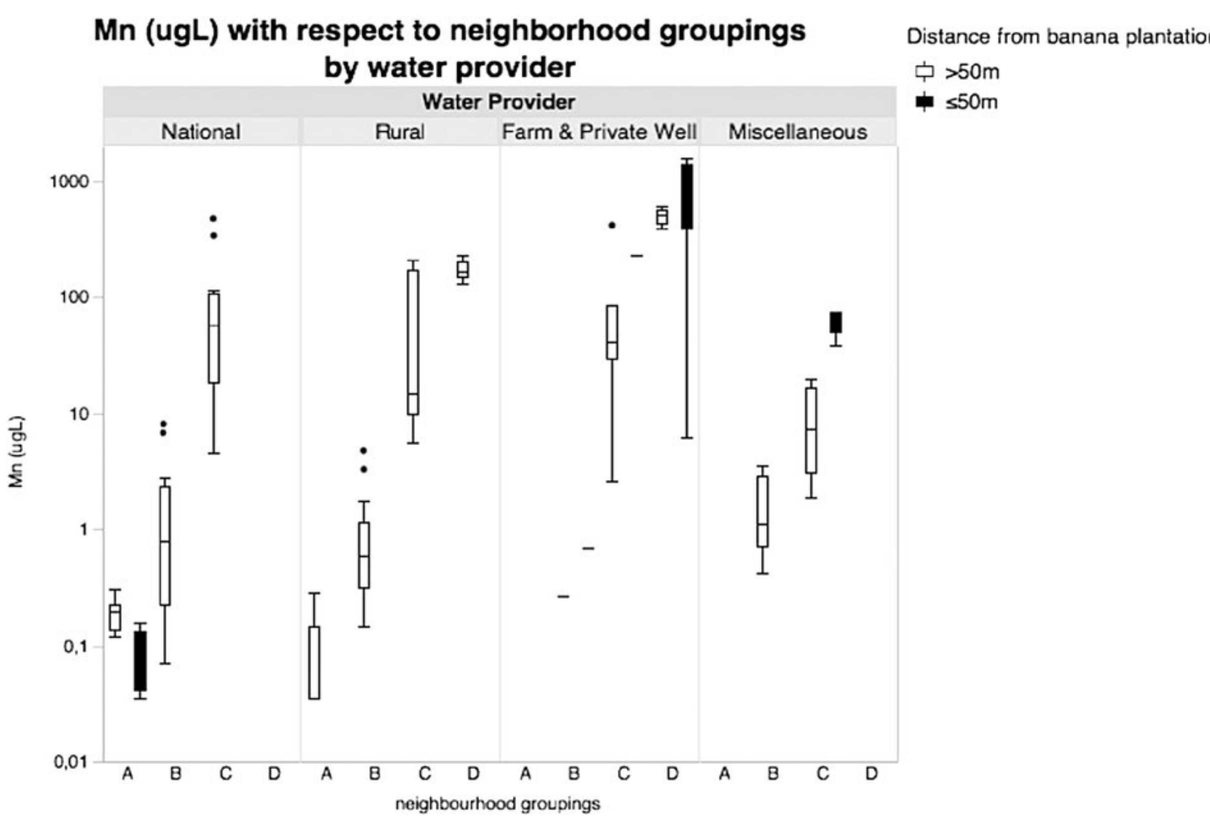

Fig. 3. Distribution of Mn with respect to neighborhood groupings, water supply systems, and distance from water source to banana plantations (<50 and ≥ 50 m).

banana plantations; drinking water samples from these systems had low Mn (median = 0.39 μg/L; max = 89.3). For the rural systems that took their water from three deep wells (30–75 m) and two wells with unknown depth located between 80 m and 2.2 km from banana plantations, there was no relation between drinking water Mn concentration and time of sampling, but there was a significant correlation with proximity to banana plantations, with the wells closest to banana plantations presenting the highest Mn (Spearman's rho = 0.75; $p < 0.001$).

Fig. 3 shows that all banana farm wells and five (28%) of the private wells were located <50 m from a banana plantation. The median Mn concentration of the private wells at <50 m distance was 1093 μg/L (range = 0.70–1599), while those farther afield had a median Mn concentration of 86 μg/L (range = 0.27–597).

With respect to the drinking water samples collected from the miscellaneous sources, the highest Mn concentrations were observed in water transported in water trucks (median = 62.0 μg/L; range = 38.2–74.8). Water was trucked from the national system deep well with the lowest Mn concentrations (median = 0.07 μg/L, range = 0.04–0.15; Fig. 3), located 24 m of the banana plantation and transported to homes that did not have access to drinking water, situated between 4 and 100 m away from banana plantations. Mn concentrations in not-transported and transported samples were, respectively: median = 0.07 μg/L (range = 0.04–0.15) and median = 62.0 μg/L (range = 38.2–74.8), almost a 1000-time increase in Mn concentrations. In contrast, Fe concentrations in not-transported and transported water samples were similar (median = 191 μg/L, range = 168–221; median = 165 μg/L, range = 132–195, respectively). Other samples within the category of miscellaneous sources included rainwater and streams had Mn concentrations <20 μg/L. The sample closest to a banana plantation (~138 m) consisted of collected rainwater, while the other sources were 1256–4233 m from banana plantations.

3.4. Socio-demographic determinants

Associations of socio-demographic characteristics of participants living in the neighborhood groupings identified in Fig. 3 were associated with metals' content in their drinking water. No differences in Mn concentration were observed for age, education, and income (data not reported); however, immigrants from other Central American countries (n = 18) were living primarily in communities from groups C (50%) and D (22%). Furthermore, more immigrants resided <50 m from a banana plantation compared to Costa Rican born (53% vs 7.6%). Median Mn concentration in immigrants' drinking water was 61.7 μg/L compared to 3.0 μg/L for Costa Rican born (p = 0.02). Median Fe value for immigrants' drinking water was 184 μg/L compared to 124 μg/L (p = 0.02). Concentrations of As and Pb did not vary by immigrant status.

4. Discussion

4.1. Most important findings

The findings of this study, conducted in an area surrounded by banana plantations with frequent aerial mancozeb spraying, show that ETU concentrations in drinking water were above the LOD (0.15 μg/L) in 6% of the samples, whereas 94% of the samples had detectable Mn (LOD = 0.05 μg/L). Thirty-three percent of the water samples had Mn concentrations >50 μg/L, 22% had concentrations >100 μg/L, and 7% had concentrations >500 μg/L. Mn concentrations were highest in drinking water samples obtained from private and banana farm wells. Distance from a banana plantation was inversely associated with Mn, Fe, and As water concentrations; this association was strongest for Mn with a 61.5% decrease in Mn concentration for each km increase in distance. Mn concentrations in water that was transported by water trucks from one village to another were almost 1000 times higher compared to water obtained from taps in houses supplied by the same well but not transported, whereas Fe concentrations did not increase, evidencing environmental contamination with Mn.

Mn in drinking water can originate from natural sources within the bedrock (Barbeau et al., 2011; Frisbie et al., 2012; Wasserman et al., 2006), from external environmental contamination (Frisbie et al., 2012; Gunier et al., 2013; Mora et al., 2014), or from intensive agriculture (Jahangir et al., 2012). Results of the present study suggest that all these sources may contribute to Mn in drinking water in the study area.

4.2. Manganese from natural sources

Mn in drinking water can originate from natural sources within the bedrock, in particularly water from deep wells (Barbeau et al., 2011; Wasserman et al., 2006; Frisbie et al., 2012). The predominant soil mineralogy of the banana production area on the Atlantic coast of Costa Rica is quartz, volcanic amorphous materials and calcium carbonate within the coarse fraction of the soil, with secondary minerals: allophane, imogolite, kaolinite, vermiculite, and sesquioxides (Gauggel et al., 2003). In the banana zones of the Atlantic Coast of Costa Rica, in soil solutions, there can be high concentrations of soluble Fe and Mn and exchangeable aluminum concentrations can be more than 30% (Gauggel et al., 2003).

Geissen et al., (2010) who studied Mn in soil and water in banana plantations and agro forestry systems in Mexico after 10 years of spraying with mancozeb, found higher concentrations of Mn were observed in soil (0–10 cm and 10–30 cm) in the areas with mancozeb spaying compared to the areas with no spraying, suggesting environmental Mn contamination from mancozeb. The authors also reported high Mn concentrations (mean ± SD = 2400 μg/L ± 100) in five deep wells (70–80 m). Yet, the Mn in these deep wells may be due to natural sources, since no differences were observed between wells and the groundwater table was separated from the subsurface water body by a layer of impermeable clay. Although Geissen et al. (2010) did not measure Mn in tap water from homes; the authors mentioned that the water from deep wells that they sampled was used for human consumption. In the present study, Mn concentrations in drinking water from deep wells (range = 0.04–475 μg/L), which may also originate in the bedrock, were considerably lower than those reported by Geissen et al. (2010).

While in this study, overall, drinking water that was supplied by the national and the rural distribution systems had low Mn concentrations, there were, in both systems, deep wells with relatively high levels of Mn, suggesting that natural Mn in groundwater contributes to the Mn in drinking water from deep wells. While some homes supplied by the same deep well showed little variability, others presented a wide range of Mn concentrations. It is noteworthy that water from the deep well of the national system with the highest Mn concentration, displayed a decrease in Mn concentration in drinking water samples over the course of the day. Barbeau et al. (2011), who examined Mn in drinking water from eight groundwater wells, reported a 36% decrease in Mn concentration over a 9-h period in one well; the authors attributed this decrease to particulate Mn within the drinking water. In the present study, while measurements were not made from the same tap throughout the day, a similar decrease was observed with respect to the time of sampling. The reason for such phenomenon is most likely due to the fact that Mn in drinking water can be found both as dissolved (Mn(II)) and particulate (Mn(IV)) form. In distribution systems, the latter is prone to deposition or re-suspension depending on the water velocity (i.e. water demand) (Carrière et al., 2005).

4.3. ETU, mancozeb spraying and manganese

In this study, ETU was only detected in a few drinking water samples (6%). Geissen et al., 2010 found elevated ETU in surface and subsurface water in a banana plantation region extensively sprayed with mancozeb compared to water samples from other areas; there was no detectable ETU in the deep wells. In water, mancozeb is quickly hydrolyzed (half-life <2 days), into ETU, which in turn is degraded to ethyl urea within a few days (Xu, 2000). In soil, mancozeb has low persistence (half-lives <2–8 days in aerobic and anaerobic soils, respectively) (Xu, 2000). It is possible that, in the present study, ETU had a low detection frequency because of its instability in water, and particularly under tropical conditions (Ruiz Suárez et al., 2013).

Our findings suggest that there may be Mn contamination of drinking water resulting from mancozeb spraying of bananas. In 2013, banana plantations in Costa Rica covered ~40,000 ha and were primarily located in the Atlantic region (CORBANA (Corporación Bananera Nacional), 2015). Weekly aerial mancozeb applications result in approximately 26 kg active ingredient/hectare/year of mancozeb being sprayed on banana plantations (Bravo et al., 2013), representing~1 million kg/year of mancozeb for the whole banana growing area. Since mancozeb is ~20% Mn by weight, it could be estimated that an amount of 208,000 kg Mn/year is applied in 40,000 ha, or 520 mg Mn/m^2/year. Using the yearly quantity of Mn deposition and assuming (i) an average annual precipitation of 3500 mm (IMN (Instituto Meteorológico Nacional), 2005) and (ii) 100% transport of mancozeb-derived Mn (a conservative hypothesis), we calculate that groundwater recharge through rainfall could potentially transport up approximately 150 μg Mn/L in groundwater from mancozeb spraying. This calculation assumes that Mn is entirely available, which is necessarily not the case as a portion of Mn is expected to precipitate or sorb onto the soil particulate matter. Nevertheless, this amount would still be insufficient to explain the high Mn in the drinking water obtained from some of the deep wells. Yet, in the present study, the highest concentrations of Mn are observed in drinking water from wells operated by banana farm companies and private wells located <50m away from banana plantations, generally dug wells 3–10 m deep. Many of the private wells were left open from time to time and Mn from mancozeb could be directly deposited into open wells or containers during spraying. Mn could also leach through the soil and be deposited into the shallow wells. In addition, there may be run-off into the wells due to the heavy rains that can flood the wells. A further route of external Mn contamination seems to occur during the transportation of water nearby the plantation area. There was an important increase in Mn content in the drinking water that is delivered by water trucks. Although the initial Mn water content is very low (median 0.07 μg/L), the water, loaded from a well embedded in a banana plantation and delivered to homes that are within 4–100 m of banana plantations, can attain 75 μg/L. External Mn contamination could occur at several points in handling and transport, for example, by mancozeb spray drift or Mn-containing dust particles.

4.4. Manganese and intensive agriculture

A third explanation for elevate Mn in drinking water may be intensive agriculture. The concentration of Mn in groundwater is controlled by the redox conditions of the aquifer and the availability of Mn within the geological deposits. Redox conditions of the aquifer will be controlled to a large extent by the microbial activity which consumes oxygen and favors reduced conditions propitious to the dissolution of Mn(II). Consequently, in the present study the higher Mn concentrations detected in shallow wells close to banana plantations could also be the result of redox modifications of the aquifer resulting from intensive agriculture (Jahangir et al., 2012). This hypothesis is supported by the observation that wells close to the banana plantations have a lower pH and higher iron content. The lower pH is coherent with increased biodegradation leading to the formation of CO_2 (an acid) while the higher concentrations of iron, a natural element also impacted by redox conditions, likewise suggests that natural Mn could also be mobilized in these wells.

4.5. Limitations and strengths

A limitation of this study was its small sample size. Water samples were only obtained from the homes of 124 (28%) of the 451 ISA study participants, resulting in relatively few samples from banana farm and private wells (n = 23) and other categories. In addition, the sampling strategy was by convenience, and therefore not necessarily representative of the entire study population. However, pregnant women that were included in this water sampling study had similar distributions of age, educational level, country of birth, and residential distance from banana plantations compared to all ISA study participants.

This study is one of the few that has explored determinants of Mn concentrations in drinking water from agricultural areas. In addition, the different approaches that we choose to analyze our data (linear multiple regression analyses and partition modeling), allowed us to identify general factors that were associated with drinking water Mn concentrations (distance from a banana plantation and water distribution system), but also to separate the different conditions and situations with respect to neighborhood groupings of Mn concentrations within each water distribution system, and explore the factors that influence Mn concentrations more closely.

4.6. Drinking water risk assessments for mancozeb

To date, drinking water risk assessment for mancozeb is based solely on ETU. The 2005 fact sheet from the United States' Reregistration Eligibility Decision (RED) for mancozeb, case number 0643 (U.S. EPA (U.S. Environmental Protection Agency), 2005a,b), states: *"drinking water exposure assessment for mancozeb addresses concentrations of ETU only, since mancozeb is not expected to remain in drinking water long enough to reach a location that would supply water for human consumption, whether from surface or groundwater sources. Estimated concentrations of ETU, for both surface and ground water sources of drinking water, are low and not of concern"*. However, the rapid decomposition of mancozeb also releases Mn into the soil and sediments (Geissen et al., 2010). Nevertheless, the potential risks associated with elevated Mn concentrations in water following mancozeb spraying (or other Mn-containing fungicides) have not been examined. This exploratory study provides some insight into Mn exposure in a region with Mn-based pesticide use. In order to elucidate the contribution of Mn-based pesticides and natural Mn to elevated Mn in drinking water in homes that are located close to fields and plantations, comprehensive studies of the pathways of exposure should be undertaken.

From a health standpoint, the ISA study, an ongoing cohort study in the region, has shown a strong association between Mn in drinking water and hair Mn concentrations (Mora et al., 2014). Other studies have reported positive correlations between Mn concentrations in drinking water and hair Mn (Bouchard et al., 2006, 2011; Phan et al., 2013). Several studies have shown associations of impaired children's neurodevelopment (Oulhote et al., 2014; Khan et al, 2012; Bouchard et al., 2006, 2011; Sahni et al., 2007; Wasserman et al., 2006; Woolf et al., 2002; Zhang et al., 1995; He et al., 1994) and neurological signs in older adults (Kondakis et al., 1989) with Mn in drinking water at levels in the range of those observed in the present study.

In July 2011, the WHO removed manganese from its Guidelines for Drinking Water Quality (WHO, 2011) arguing that the previous recommendation of 400 μg/L was *"well above concentrations of manganese normally found in drinking water*". Several scientists contested this decision and provided a list of 54 countries with documented or potential drinking water sources containing Mn concentrations above this level (Frisbie et al., 2012). In the present study, 9.5% of the drinking water samples surpassed this value, supplying additional evidence that elevated Mn drinking water concentrations also occur in the Atlantic region of Costa Rica.

It is noteworthy that, in the present study, there were more immigrants living in close proximity to the banana plantations and their drinking water had higher Mn concentrations compared to the non-immigrants, raising the question of social equity and environmental justice. Inequality in access to piped-in drinking water has been shown to exist in many countries (Yang et al., 2013). Agricultural workers and their families, particularly but not exclusively in low income countries, often have poor access to piped-in water and live close to areas where pesticides are sprayed, potentially contaminating their drinking water. In Costa Rica and in other countries in which communities' water supply is provided by individual and industry-owned wells, drinking water should be monitored for Mn and other potential contaminants.

4.7. Conclusions and recommendations

We conclude that elevated Mn in drinking water in this area of Costa Rica is likely to originate from both groundwater and external contamination, probably due to mancozeb spraying. In Costa Rica, pilots who apply pesticides using light aircrafts must maintain a distance of 100 m from residential areas in absence of a natural vegetative barrier, such as trees, and 30 m in presence of a natural vegetative barrier (LA GACETA, 2008). However, those distances are not always respected (Barraza et al., 2011) or may be insufficient to prevent off-target pesticide drift (van Wendel de Joode et al., 2014). Intensive agriculture with extensive mancozeb use may also contribute to elevated Mn concentrations in drinking water.

Mancozeb is extensively used worldwide and further studies should examine its possible contribution to elevated Mn in drinking water. Mn is a well-known neurotoxin; several studies have shown negative associations between Mn in drinking water and children's cognition and behavior at concentrations similar to those observed in the present study. The findings of this study support the need for health-based WHO guidelines on Mn in drinking water. Finally, in order to lower Mn intake in populations who drink water from private and banana farm wells and prevent possible health effects due to elevated Mn, it is necessary to examine the feasibility of extending national and rural water supply systems to these communities. On the short term, infrastructure of existing wells and the management of drinking water during its transport should be improved to decrease contamination.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.04.015.

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