Metal uptake in maize, willows and poplars on impoldered and freshwater tidal marshes in the Scheldt estuary

B. Vandecasteele[1], C. A. Buysse[1] & F. M. G. Tack[2]
[1]*Institute for Forestry and Game Management, Ministry of the Flemish Community, Gaverstraat 4, B-9500 Geraardsbergen, Belgium, and* [2]*Department of Applied Analytical and Physical Chemistry, Ghent University, Coupure 653, B-9000 Ghent, Belgium*

Abstract

Foliar Cd and Zn concentrations in *Salix*, *Populus* and *Zea mays* grown on freshwater tidal marshes were assessed. Soil metal concentrations were elevated, averaging 9.7 mg Cd kg^{-1} dry soil, 1100 mg Zn kg^{-1} dry soil and 152 mg Cr kg^{-1} dry soil. Cd (1.1–13.7 mg kg^{-1}) and Zn (192–1140 mg kg^{-1}) concentrations in willows and poplars were markedly higher than in maize on impoldered tidal marshes (0.8–4.8 mg Cd kg^{-1} and 155–255 mg Zn kg^{-1}). Foliar samples of maize were collected on 90 plots on alluvial and sediment-derived soils with variable degree of soil pollution. For soil Cd concentrations exceeding 7 mg Cd kg^{-1} dry soil, there was a 50% probability that maize leaf concentrations exceeded public health standards for animal fodder. It was shown that analysis of foliar samples of maize taken in August can be used to predict foliar metal concentrations at harvest. These findings can therefore contribute to anticipating potential hazards arising from maize cultivation on soils with elevated metal contents.

Keywords: Exposure assessment, biological monitoring, wetland, sediments, *Salix*, cadmium, zinc, chromium

Introduction

Sediment-derived soils are likely to contain metal levels above normal baseline concentrations in upland soils. In Flanders, Belgium, elevated metal concentrations were encountered in tidal marshes (Vandecasteele *et al.*, 2004), and in alluvial soils of the Scheldt River originating from overbank sedimentation (Swennen & Van der Sluys, 2002) or landfilling of dredged sediments (Vandecasteele *et al.*, 2002a). These metal concentrations may be the origin of higher metal availability to plants (Singh *et al.*, 1998; Tack *et al.*, 1998), and could lead to ecological and human risks. Tidal marshes play an important role in the sediment budget of the Scheldt estuary, because it is predominantly an embanked river.

Leaves of willow and poplar were found to be suitable bioindicators for Cd, Mn and Zn (Vandecasteele *et al.*, 2002b, 2003; Piczak *et al.*, 2003). Willows are the climax vegetation on freshwater tidal marshes (FTM) (Bal *et al.*, 2001), and in Flanders, they commonly colonize sediment-derived substrates contaminated with heavy metals (Vandecasteele *et al.*, 2002b). Willow cultures and poplar plantations were grown on FTM along the Sea Scheldt (Temmerman *et al.*, 2003a). Although these economic activities have ended, remnants of these cultures remain.

Tidal flats in the Scheldt estuary have been reclaimed for agriculture after impoldering by dike construction (Eertman *et al.*, 2002). While polluted soils may constitute certain ecological risks, agricultural use of polluted sediment-derived soils may be unacceptable (Smilde *et al.*, 1982; Gambrell & Patrick, 1988). Elevated Cd concentrations in maize grown on polluted sediment-derived sites have been reported by several authors (e.g. van Driel *et al.*, 1995). Maize accumulates more Cd in roots than in aboveground parts (Guo *et al.*, 1996; Lozano-Rodriguez *et al.*, 1997; Joner & Leyval, 2001; Nigam *et al.*, 2001). In contrast, concentrations of Zn are highest in leaves, intermediate in stems and roots, and lowest in the cobs (Wenger *et al.*, 2002). In a field trial with artificially contaminated soils, Bourrie *et al.* (1998) noticed that maize grain concentrations were low compared with concentrations measured in the other aboveground parts. In contrast to other crops, the pollution status of the soil has only a limited influence on maize growth and yield (Lozano-Rodriguez *et al.*, 1997; Bourrie *et al.*, 1998; Wenger *et al.*, 2002).

The aim of this paper was to determine metal concentrations in maize, willows and poplars growing on natural or impoldered FTM. In the first part of the study, trees and crops were sampled at 16 plots. The second part focuses on permissible Cd concentrations in maize grown in polluted sediment-derived soils. The data from this study have been used to derive maximum permissible Cd concentrations in farmed alluvial soils and to establish if Cd concentration in maize foliage sampled in August gives a good prediction of concentration at harvest.

Materials and methods

Foliar and soil sampling on freshwater tidal marshes

In the first part of this study, 13 plots on intact FTM and three plots on impoldered FTM along the Sea Scheldt River were sampled (Figure 1, Table 1). In the Scheldt estuary, FTM with willow woods occur as a climax stage between the Rupel and the Dender embouchures, and along the Durme tributary, whilst salt marshes dominate downstream from the Rupel (Van den Bergh *et al.*, 1999). The impoldered FTM currently function as stormwater floodplains at spring tides and are used for maize monoculture. The natural FTM are regularly flooded at high tide. Flooding frequency and sedimentation rates are related to surface elevation and distance to the nearest creek or marsh edge (Temmerman *et al.*, 2003b). A plot is defined in this text as a location of 80 m^2 with relatively homogeneous soil properties where four trees or shrubs of the same species were sampled or four samples of maize (sampling area restricted to 3.1 m^2) were collected. For plot 13, only three trees could be sampled.

For poplars and willows, at least four branches from different heights and positions in the crown of similar age and size were sampled. Samples were taken in the second half of August (week 33) by means of a large catapult (Mathias, 2001) for taller trees (>10 m), or with an extension crosscut saw for trees smaller than 10 m (Blair, 1995). Sampling was repeated at the end of the growing season (week 42, second half of October) when intensive foliar paling was noticed. Approximately 500 cm^3 of leaves were collected per tree at each plot. Four random composite samples of maize leaves were collected in a circle of 2 m diameter in week 33. Excessive dust was removed from the samples, but the leaves were not washed to comply with food chain research protocols (Ernst, 1990). The leaves were dried for 7 days at 40 °C, mechanically ground (Pulverisette 14; Fritsch, Idar-Oberstein, Germany) and stored in dark glass vials before analysis. At each plot, the soil was sampled (0–30 cm) in quadruplicate with an Edelman auger for physical and chemical characterization. All soil samples were dried at 40 °C until constant weight and ground to pass a 2-mm sieve with a heavy metal-free, high-grade stainless steel mechanical grinder (Retsch, Haan, Germany).

Maize and soil sampling on alluvial soils

In the second part of this study, foliar samples of maize were collected in the second half of August (week 33) from 90 plots on uncontaminated alluvial soils and contaminated sediment-derived soils along the Upper and Sea Scheldt, the Leie and Durme river and along the Ghent-Bruges canal (Figure 1). Maize leaves (500 cm^3) were collected at random in a circle of 2 m diameter around the point where the A horizon was sampled. Thickness of the A horizon varied

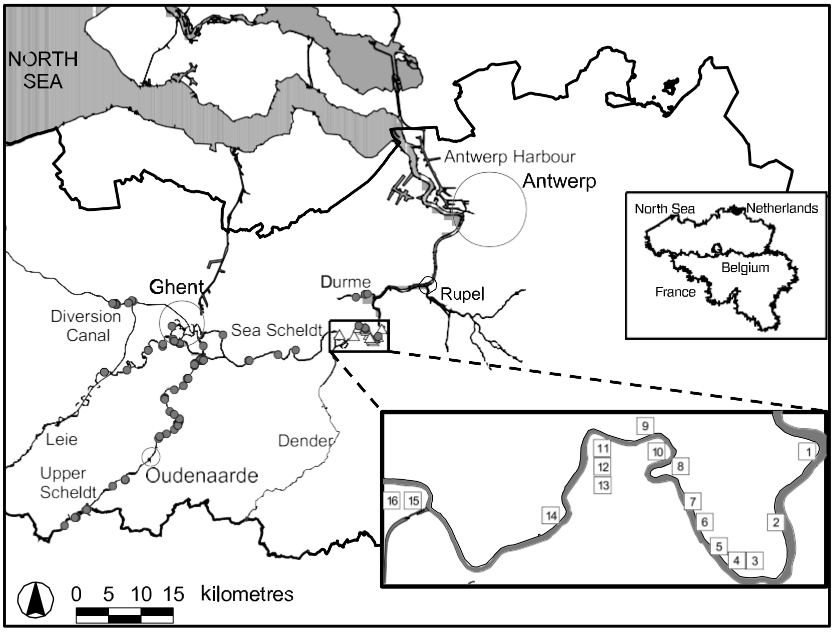

Figure 1 Locations of the 16 plots on freshwater tidal marshes where maize, willows and poplars were sampled (triangles and numbered squares) and the 90 plots where maize was sampled (circles).

Table 1 Sampled species and number of sample replicates collected in week 33 and week 42 on 16 plots on freshwater tidal marshes. Numbered plots are shown in Figure 1

		Number of samples	
Plot	Species	Week 33	Week 42
1	*Salix triandra* (L.)	4	4
2	*Zea mays* (L.)	4	
3	*Salix viminalis* (L.)	4	4
4	*Salix cinerea* (L.)	4	4
5	*Populus deltoides* (Marsh.) · *P. nigra* (L.)	4	4
6	*Salix triandra* (L.)	4	4
7	*Salix fragilis* (L.)	4	4
8	*Salix dasyclados* (Wimm.)	4	4
9	*Zea mays* (L.)	4	
10	*Zea mays* (L.)	4	
11	*Salix viminalis* (L.)	4	4
12	*Populus deltoides* (Marsh.) · *P. nigra* (L.)	4	4
13	*Salix cinerea* (L.)	3	3
14	*Salix triandra* (L.)	4	4
15	*Salix viminalis* (L.)	4	4
16	*Populus deltoides* (Marsh.) · *P. nigra* (L.)	4	4

between 25 and 45 cm. To assess the variability in maize foliage, 18 locations were sampled with this methodology in quadruplicate. To assess temporal variability in foliar concentrations and concentration differences between leaves and stems, two polluted plots were sampled with four replicates both in week 33 and week 39 (last week of September, harvest period), and maize stems (stem part between 50 and 100 cm height) were collected in week 39.

Chemical analysis

Total foliar element concentrations were extracted with HNO_3 (p.a. 65%) and H_2O_2 (ultrapur) in a 3:1 ratio using microwave digestion (Milestone 1200 MS Mega) and measured with ICP-AES (Varian Liberty Series II; Varian, Palo Alto, CA, USA). The accuracy of the element analyses was checked using BCR 60 (aquatic plant) for Cd, Cu, Mn and Zn and CRM 100 (beech leaves) for Ca, Mg, Na, K, S and P.

Soil pH_{H_2O}, pH_{CaCl_2} and electrical conductivity (EC) were measured in a 1:5 soil to water suspension. Organic carbon (OC) was determined by the method of Walkley-Black, assuming that this method measures 75% of the total OC (TOC). $CaCO_3$ content was determined by back-titration with 0.5 m NaOH of an excess of H_2SO_4 added to 1 g air-dried sediment. TOC in soil was measured with a TOC analyser equipped with a solid sample module operational at 900 °C (Shimadzu 5050A Solid Sample Module Analyser; Shimadzu, Kyoto, Japan). The particle size distribution of the soil samples was determined using laser diffractometry (Coulter LS200, Miami, FL, USA) with the clay fraction defined as the 0–6 lm fraction (Vandecasteele *et al.*, 2002a). Soil total contents of Cd, Cr, Cu, Ni, Pb, S, P and Zn are pseudo-total *aqua regia* extractable contents measured with ICP-AES after microwave digestion.

Statistics and permissible levels

Bioconcentration factors (BCF) for Cd and Zn on a dry weight basis were defined as the ratio of foliar concentration to total soil concentration (*aqua regia*). Foliar concentrations for Cd, Zn, Mn, Fe and Cu for week 33 and week 42 were compared in pairs with the paired *t*-test at the 95% level of significance for the four trees sampled at each plot.

Willow and poplar leaves entering the biogeochemical cycle during autumn can be seen as a fertilizer application, and thus threshold concentration values of 6 mg Cd kg$^{)1}$ dry weight (DW), 375 mg Cu kg$^{)1}$ DW and 900 mg Zn kg$^{)1}$ DW as imposed in Flemish legislation (VLAREA, 2004) may be used. Maximum annual applications are 1.2 mg Cd m$^{)2}$, 75 mg Cu m$^{)2}$ and 180 mg Zn m$^{)2}$ (VLAREA, 2004). Maize is cultivated in Flanders mainly as fodder (forage maize for silage). Current legislative standards are based on EU directive 1999L0029 (Council Directive, 1999) adopted in Belgian legislation (BS 21/04/99). In fodder of vegetable origin with a water content of 12%, the maximum permissible level is 1 mg Cd kg$^{)1}$, or 1.14 mg Cd kg$^{)1}$ on a DW base. There are no legislative standards for Cu and Zn in fodder. Normal Cd and Zn foliar concentrations in maize were estimated from the range determined in maize sampled on 29 plots with soil concentrations <0.7 mg Cd kg$^{)1}$ dry soil and <150 mg Zn kg$^{)1}$ dry soil. Normal concentrations in poplars were derived from Vandecasteele *et al.* (2003). Because a large difference was found in foliar Cd and Zn concentrations between tree and shrub willows with higher values for the latter (Granel *et al.*, 2002), normal concentrations for tree willows were based on Vandecasteele *et al.* (2002b), and for shrub willows on data from Severson *et al.* (1992).

The relationship between soil and plant Cd and Zn concentrations in maize was tested with linear regression after both concentrations were log-transformed. The Cd concentrations in the maize leaves were divided into 20 classes based on the soil concentration. For each class the probability of exceeding the public health standards was assessed from a histogram to determine the soil concentration with a 50 and 90% probability of exceeding the standard. Two-way ANOVA was used to determine differences between foliar concentrations in week 33 and week 39 for the two plots, and the *t*-test was used for testing the difference between stem and foliar concentrations in maize.

Pearson correlation coefficients were calculated between metal concentrations in poplar and willow leaves on the one hand, and plot elevation and distance to the river on the other. Elevation of the plots was derived from the OG-GIS digital elevation model for Flanders (OC-GIS Vlaanderen, 2004). Distance from a plot to the river was calculated perpendicularly to the axis of the Scheldt River.

Results

Plant metal uptake on freshwater tidal marshes

Soil metal concentrations in the FTM were elevated compared with normal baseline concentration levels in Flanders (90th percentile values are 0.6–2, 37–77 and 56–100 mg kg^{-1} for Cd, Cr and Zn respectively; Tack *et al.*, 1997) (Table 2). Plots were generally characterized as calcareous soils with high clay contents. The low EC values illustrate that the plots were on freshwater marshes. Overall, properties and pollution status were similar for the 16 sampled plots (Table 2).

In general, normal to slightly elevated foliar Cd and Zn concentrations were measured relative to normal concentrations for poplars, tree and shrub willows (Table 3). Exceptions for Cd are plots 12, 13 and 16, and for Zn plots 13 and 16. Permissible levels for Cd in fodder were exceeded for the three sampled plots in maize. For four of the 13 plots with poplars or willows, foliar concentrations in week 33 were above permissible Cd levels, and half of the plots were above this level in week 42 (Figure 2). For Zn, two of the 13 plots with willow or poplar had foliar concentrations exceeding the threshold value for fertilizer application (Figure 2). Cu concentrations in the leaves were well below the permissible level. The calculated annual metal input, assuming 260 g m^{-2} leaf fall as an average value for fullgrown *Salix alba* stands, did not exceed the maximum annual application dose for Cu in any plot, but maximum allowable doses were exceeded for Cd on plots 4, 12, 13, 15 and 16, and for Zn on plots 12, 13 and 16.

Comparison of foliar concentrations in week 33 and week 42 for willows and poplars reveals, for half of the plots, a distinct increase of Cd and Zn, while Fe and Mn concentrations were more or less constant. Variable trends were noticed for the generally low Cu concentrations in the leaves.

Permissible Cd levels in forage maize

The sampled alluvial soils have a broad range of metal concentrations for Cd, Cr and Zn (Table 4), and were in general calcareous. The relative standard deviation (RSD, otherwise denoted as the coefficient of variation) for foliar Cd and Zn in maize leaves for four replicates on 18 plots varied between 2.1 and 39.8% with an outlier of 57.6% for Cd and between 6.2% and 34.3% for Zn. The RSD was therefore acceptable (Figure 3). For both Cd and Zn, there was a strong positive correlation between foliar (mg kg^{-1} DW) and total soil (mg kg^{-1} dry soil) concentrations (Figure 4):

$$\log(\mathrm{Zn_{leaves}}) = 0.417 + 0.603 \times \log(\mathrm{Zn_{soil}}); \quad P < 0.0001; R^2 = 0.71; \tag{1}$$

$$\log(\mathrm{Cd_{leaves}}) = -0.463 + 0.667 \times \log(\mathrm{Cd_{soil}}); \quad P < 0.0001; R^2 = 0.610. \tag{2}$$

Overall, the comparison showed no significant differences ($P > 0.05$) between foliar Cd and Zn concentrations in week 33 and week 39, although average Cd concentrations were

Table 2 Soil characteristics (on a dry weight basis) of the 16 plots on freshwater tidal marshes where poplar, willow or maize was sampled

Plot	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})	P (g kg^{-1})	Mn (g kg^{-1})	Fe (g kg^{-1})	$CaCO_3$ (%)	pH_{H_2O}	EC (μS cm^{-1})	TOC (%)	Clay (%)
1	10.3 (3.3)	220 (41)	147 (20)	1030 (194)	4.9 (0.4)	1.3 (0.1)	46.9 (2.8)	8.8 (0.2)	7.8 (0.1)	270 (25)	6.5 (0.4)	50 (2)
2	11.3 (1.3)	382 (49)	106 (8)	1169 (81)	3.2 (0.2)	0.8 (0)	36.5 (1.8)	6.9 (0.3)	7.8 (0)	171 (8)	3.8 (0.2)	36 (2)
3	11.7 (3.3)	156 (5)	300 (112)	1303 (260)	5.4 (0.2)	1.7 (0.1)	49.2 (1.3)	9.4 (1.3)	7.7 (0)	272 (16)	6.8 (0.3)	53 (2)
4	10.7 (4.5)	170 (88)	211 (147)	1120 (295)	4.4 (0.5)	1.3 (0.3)	43.4 (1)	9 (1.3)	7.7 (0.1)	262 (54)	5.5 (0.9)	46 (2)
5	10.6 (3.1)	113 (31)	202 (134)	1045 (271)	3.6 (0.8)	1.1 (0.3)	35.7 (7.2)	5.7 (1.2)	7.9 (0.1)	292 (16)	6.4 (1.1)	38 (9)
6	9.9 (2.1)	139 (16)	202 (28)	1097 (157)	4.4 (0.7)	1.5 (0)	41.4 (6.6)	9.8 (1)	7.8 (0.1)	277 (17)	7.2 (1.4)	49 (1)
7	6.5 (0.8)	100 (6)	95 (5)	852 (99)	3.1 (0.1)	1.5 (0.2)	41.5 (2.5)	8.7 (0.4)	7.9 (0.1)	229 (31)	5.9 (0.4)	43 (3)
8	11.6 (3.8)	166 (18)	250 (23)	1202 (219)	5.4 (0.4)	1.5 (0.1)	46.5 (1.1)	8.4 (0.2)	7.6 (0.1)	257 (18)	7.1 (0.5)	48 (2)
9	12.2 (0.6)	399 (6)	133 (3)	1601 (38)	3.4 (0.1)	0.7 (0)	35.3 (1.2)	7.4 (0.2)	7.6 (0.1)	156 (8)	4.8 (0.2)	39 (1)
10	15.8 (0.1)	454 (4)	157 (1)	1723 (18)	4.5 (0.1)	0.8 (0)	41.3 (1)	7.2 (0.5)	7.6 (0.2)	184 (13)	4.6 (0.2)	43 (1)
11	11 (2.6)	163 (16)	275 (62)	1262 (166)	5.2 (0.4)	1.8 (0.1)	47.9 (4)	8.9 (0.6)	7.6 (0)	283 (12)	7.8 (0.8)	53 (2)
12	8.3 (1.5)	100 (10)	145 (61)	987 (134)	3.7 (0.2)	0.9 (0.1)	34.6 (2.1)	7.9 (0.4)	7.6 (0)	192 (15)	4.3 (0.2)	38 (2)
13	10.2 (1.2)	154 (4)	256 (19)	1253 (130)	5 (0.2)	2 (0.2)	47.5 (0.8)	9.1 (0.3)	7.7 (0)	265 (22)	7.2 (1.4)	53 (2)
14	10.1 (1.5)	145 (17)	277 (26)	1241 (124)	4.8 (0.5)	2 (0.6)	47.7 (0.7)	8.6 (0.6)	7.7 (0.2)	340 (28)	8.5 (0.7)	48 (2)
15	13.2 (2.2)	133 (7)	346 (88)	1684 (191)	4.4 (0.1)	1.1 (0.1)	40.5 (0.4)	7.6 (0.3)	7.6 (0.1)	221 (6)	6.2 (0.2)	46 (0)
16	9 (1.9)	104 (7)	151 (101)	1279 (234)	3.2 (0.9)	0.9 (0.1)	30 (7.5)	7.3 (0.2)	7.7 (0)	188 (7)	5.2 (0.2)	40 (2)

Values in parentheses are standard deviations for four replicates. For methods of analysis see Materials and methods – Chemical analysis.

Table 3 Measured, normal and permissible foliar concentrations (mg kg^{-1} dry weight) for maize, poplars and willows for 16 plots on freshwater tidal marshes. Numbered plots are shown in Figure 1, and species on the plots are listed in Table 1

	Measured					Normal		Permissible	
Plot	Cu	Fe	Mn	Cd	Zn	Cd	Zn	Cd	Zn
1	6.1	204	74.6	4.3	504	0.2–3.4	110–560	6.0	900
2	22.2	172	20.0	4.2	200	0.1–0.4	17–80	1.1	–
3	6.4	173	89.1	4.5	497	0.2–3.4	110–560	6.0	900
4	7.9	135	96.4	5.2	534	0.2–3.4	110–560	6.0	900
5	5.9	119	23.9	4.2	399	2.2–4.0	60–184	6.0	900
6	5.0	286	63.7	3.1	385	0.2–3.4	110–560	6.0	900
7	7.9	129	182.7	3.4	298	0.5–2.9	128–338	6.0	900
8	5.3	116	51.9	3.5	401	0.2–3.4	110–560	6.0	900
9	9.6	152	14.5	1.2	167	0.1–0.4	17–80	1.1	–
10	17.1	167	16.1	1.8	202	0.1–0.4	17–80	1.1	–
11	8.4	149	62.3	3.0	374	0.2–3.4	110–560	6.0	900
12	7.0	88	31.2	9.0	668	2.2–4.0	60–184	6.0	900
13	7.6	146	166.5	12.9	1138	0.2–3.4	110–560	6.0	900
14	6.8	155	228.2	1.1	192	0.2–3.4	110–560	6.0	900
15	9.4	188	39.2	6.4	436	0.2–3.4	110–560	6.0	900
16	4.1	104	35.2	13.7	1013	2.2–4.0	60–184	6.0	900

higher in week 39 (Figure 5). Therefore, foliar samples taken in week 33 allow a satisfactory assessment of foliar quality at harvest. For the two plots, a significant difference ($P < 0.05$) in Cd concentration was detected between leaf (5.2 mg Cd kg^{-1} DW) and stem (2.6 mg Cd kg^{-1} DW). Although Cd concentrations tended to be twice as high in leaves as in stems (Figure 5), there were no significant differences between stem and leaf Zn concentrations. The soil Cd concentrations resulting in a 50% and 90% probability of exceeding public health standards for animal fodder grown on the soil was 7.0 and 11.5 mg Cd kg^{-1} dry soil respectively (Figure 6). Our results indicate that health standards are not exceeded (10% and 35% probability, respectively) when soil concentrations in the A horizon do not exceed the Flemish soil sanitation standards for agricultural land-use (VLAREBO, 1996), ranging from 1.7 to 5.1 mg Cd kg^{-1} dry soil for the soil types in this study (0.5% OC and 8% clay to 9% OC and 39% clay, see 10th and 90th percentile values in Table 4).

Discussion

Plant uptake on freshwater tidal marshes

Evaluation of Cd and Zn concentrations in poplar and willow leaves is not straightforward, because foliar concentrations are highly variable even in baseline situations. In a greenhouse experiment with 15 willow clones grown in uncontaminated soil, Granel *et al.* (2002) found foliar concentrations of 1.6–10.0 mg Cd kg^{-1} DW and 60–220 mg Zn kg^{-1} DW. Foliar baseline values for Cd and Zn in willow (Nissen & Lepp, 1997; Eriksson & Ledin, 1999) and poplar leaves (Vandecasteele *et al.*, 2003) usually reflect BCF of up to 10. In contrast, BCF for willows on FTM in this study were in the range 0.1–0.5 for Cd and 0.2–0.5 for Zn, with *S. cinerea* on plot 13 having deviant BCF values of

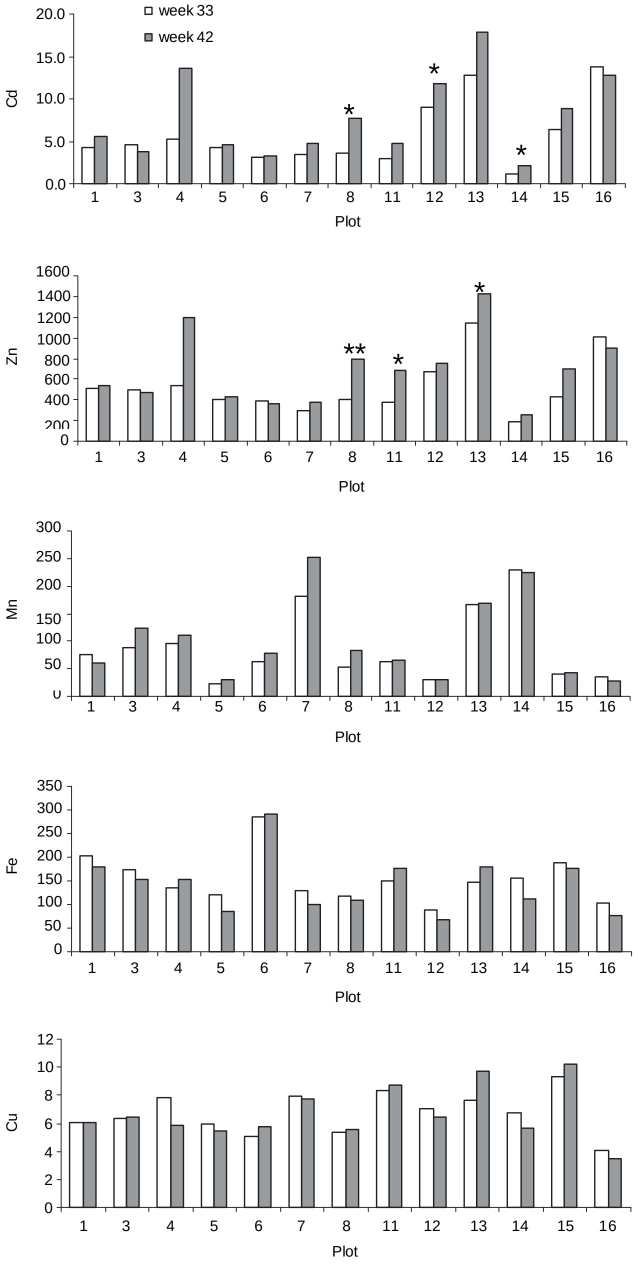

Figure 2 Foliar concentrations (mg kg^{-1} DW) of willows and poplars on polluted freshwater tidal marshes in week 33 and week 42. Significant differences detected with the paired *t*-test are indicated with *($P < 0.05$) or **($P < 0.01$). Numbered plots are indicated on Figure 1.

Table 4 Descriptive data for the soil characteristics for 90 plots where maize was sampled

	Minimum	10th percentile	Average	Median	90th percentile	Maximum
Cd (mg kg^{-1} dry soil)	0.2	0.3	5.8	2.5	22.9	29.0
Cr (mg kg^{-1} dry soil)	12	29	394	133	1545	2769
Cu (mg kg^{-1} dry soil)	5	8	72	47	154	449
Ni (mg kg^{-1} dry soil)	4	6	23	21	47	58
Pb (mg kg^{-1} dry soil)	5	10	152	100	292	771
Zn (mg kg^{-1} dry soil)	34	67	776	515	2026	3556
% clay	3	8	22	21	39	48
P (g kg^{-1} dry soil)	0.4	0.6	2.2	1.4	6.0	7.1
S (g kg^{-1} dry soil)	0.2	0.3	1.1	0.8	2.2	8.7
N (g kg^{-1} dry soil)	0.2	0.9	2.6	2.7	4.2	5.6
% $CaCO_3$	0.1	1.4	5.3	5.4	9.2	10.0
% OC	0.2	0.5	2.4	2.4	4.5	5.4
pH_{H_2O}	5.9	7.0	7.5	7.6	8.1	8.3
pH_{CaCl_2}	5.2	6.2	7.0	7.2	7.6	7.9
EC (µS cm^{-1})	34	102	276	174	547	2073

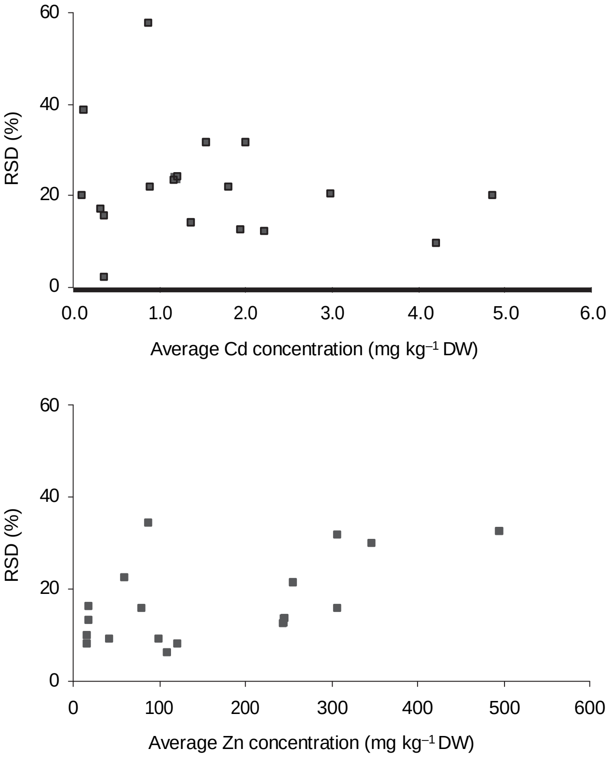

Figure 3 Relative standard deviation (RSD) for Cd and Zn concentrations in maize leaves in relation to average foliar concentrations for 18 plots sampled with four replicates.

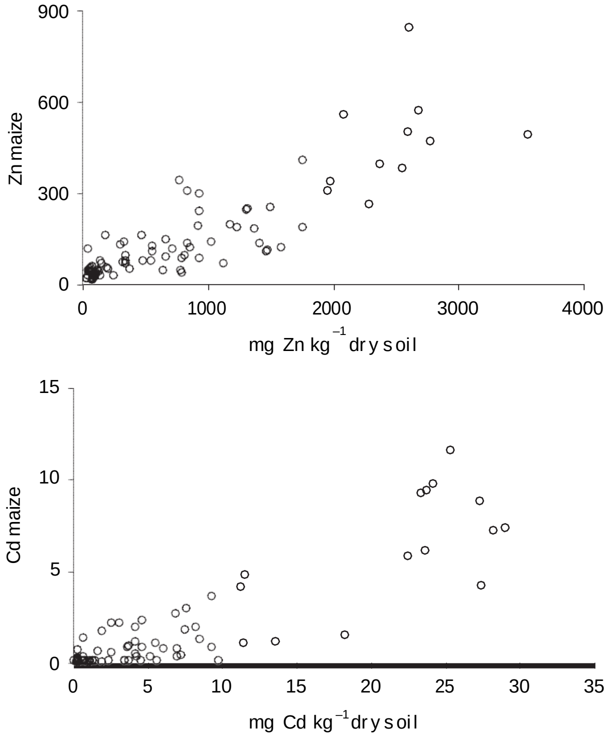

Figure 4 Cd and Zn concentrations in maize leaves (mg kg^{-1} DW) and soils (mg kg^{-1} dry soil) for 90 plots.

1.3 for Cd and 0.9 for Zn. These BCF values are substantially smaller than those found for willows on polluted dredged sediment-derived soil (Vandecasteele *et al.*, 2002b) with BCF of 0.6–2.4 for Cd and 0.4–1.0 for Zn. Therefore, Cd and Zn tend to be less available for willows on FTM than on polluted dredged sediment-derived soils. This observation is in agreement with observations of Vandecasteele *et al.* (2004). They found similar foliar Cd and Zn concentrations for *S. alba* on polluted FTM as in baseline situations, but significantly higher foliar concentrations on polluted soils on dredged sediments with comparable soil metal concentrations to the FTM. This difference might be caused by the wetter regime of the FTM, resulting in low

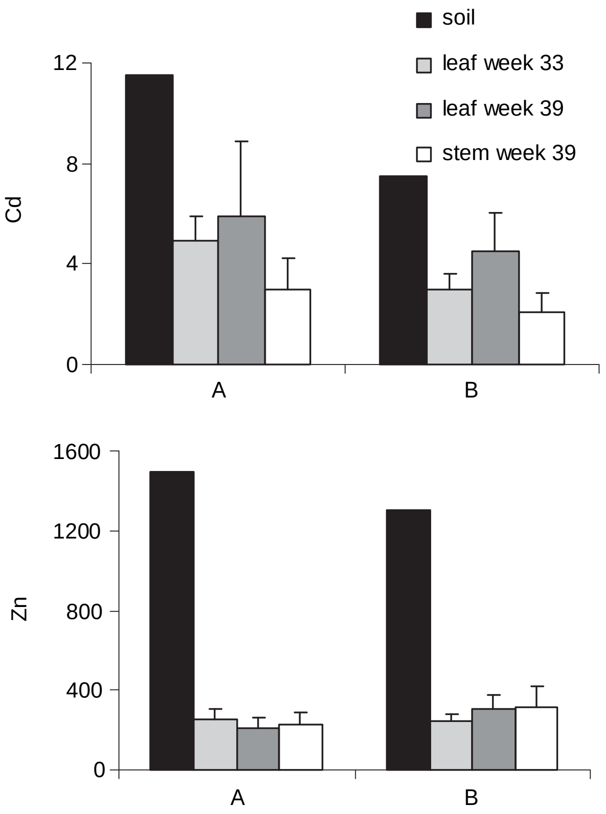

Figure 5 Total Cd and Zn concentrations in the soil (mg kg$^{)1}$ dry soil), in maize leaves collected in week 33, and maize leaves and stems collected in week 42 (mg kg$^{)1}$ DW) for two contaminated plots (A and B). Values are average of four replicates and error bars indicate the standard deviation for maize samples.

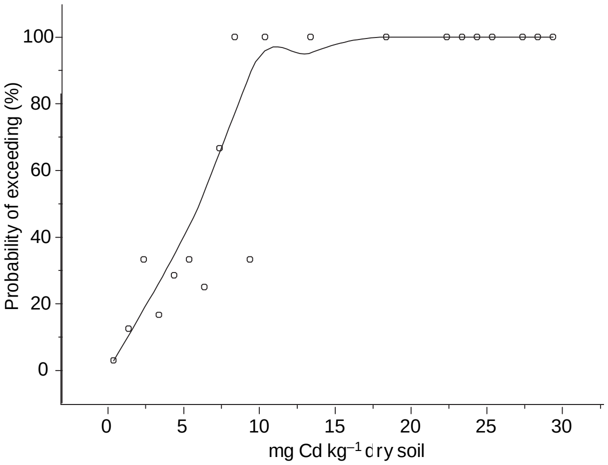

Figure 6 Probability of exceeding the public health standard for Cd in fodder in relation to soil Cd concentration.

oxidation–reduction potential (Eh) and low metal bioavailability (Gambrell *et al.*, 1991) due to tidal flooding. BCF values for poplars on FTM in this study (0.4–1.5 for Cd and 0.4–0.8 for Zn) are similar to values reported for poplars on polluted overbank sedimentation zones and dredged sediment-derived soils (0.3–1.9 for Cd and 0.1–0.6 for Zn, Vandecasteele *et al.*, 2003).

Highest foliar Cd and Zn concentrations were measured on plot 12 (*Populus* D · N), 13 (*S. cinerea*) and 16 (*Populus* D · N), located in the upstream part of the study area. These results might be caused by the plant species, soil characteristics, location within the estuary or a combination of these factors. Both soil salinity and Eh can affect metal bioavailability (Gambrell *et al.*, 1991), with increased bioavailability at higher Eh and salinity. The low EC values in Table 2 illustrate that all sampled plots were on freshwater marshes, and EC values measured on plots 12, 13 and 16 were no higher than for the other plots. Moreover, the Scheldt estuary is characterized by an increasing salinity towards the North Sea, with the least salinity in the most upstream part of the estuary (plots 12–16). Eh is affected by flooding intensity and duration and may vary during a tidal cycle. Characteristics of tidal cycles are affected by location of the plot within the estuary and vary periodically; Eh is expected to vary accordingly. The duration of the low tide during a tidal cycle increases with distance from the North Sea, which may cause longer periods of water saturation and lower Eh values in the plots furthest upstream. No significant correlation ($P > 0.05$, n ¼ 13) was found between foliar Cd (correlation coefficient r ¼ 0.15) or foliar Zn (r ¼ 0.12) and plot elevation, and between foliar Cd (r ¼)0.36) or foliar Zn (r ¼)0.22) and distance from the plot to the river. These trends indicate that higher foliar Cd and Zn concentrations in plots 12, 13 and 16 may not be caused by Eh or salinity, plot elevation or distance from the river. However, the data set is too limited to determine unambiguously whether any of these factors affect foliar concentrations.

Permissible Cd levels in forage maize

The maximum concentrations of Zn and Cd in maize leaves found in this study were 848 and 11.6 mg kg$^{)1}$ DW respectively. No direct toxic effects in maize plants were observed despite the high foliar Cd concentrations measured, which sometimes exceeded 10-fold the public health standards for animal feed. Highest reported maize Zn concentration measured in a field trial was 1665 mg kg$^{)1}$ DW (Wenger *et al.*, 2002) for an artificially contaminated soil (800 mg Zn kg$^{)1}$ dry soil). van Driel *et al.* (1995) measured maize concentrations of 1.9 mg Cd kg$^{)1}$ DW and 152 mg Zn kg$^{)1}$ DW for a calcareous dredged sediment-derived soil with 20.2 mg Cd kg$^{)1}$ dry soil and 1291 mg Zn kg$^{)1}$ dry soil. Bourrie *et al.* (1998) reported foliar concentrations of up to 7.8 mg Cd kg$^{)1}$ DW for an artificially contaminated soil with 50 mg Cd kg$^{)1}$ dry soil. Morphological toxicity symptoms (reduced shoot length and leaf yield) in *Zea mays* were observed at foliar concentrations of 123 and 73 mg Cd kg$^{)1}$

DW in the third and fourth leaf (Lagriffoul *et al.*, 1998). However, increased peroxidase activity, an early toxicity indicator, was already observed at foliar concentrations of 3–5 mg Cd kg$^{)1}$ DW (Lagriffoul *et al.*, 1998). These authors also concluded that maize was more tolerant of Cd than Cu.

In a field trial with artificially contaminated soils, Bourrie *et al.* (1998) calculated that Cd export in maize leaves, stems, grain and cobs at harvest, accounted for 56, 25, 13 and 6%, respectively, of the total Cd content in the aboveground parts. We only used maize leaves for quality assessment, but the results of Bourrie *et al.* (1998) indicate the relative importance of leaves in the total Cd export. Foliar samples taken in the second half of August can be used to assess foliar quality at harvest, making it possible to decide some weeks before harvest whether harvested maize can be used as fodder or must be incinerated as part of a phytoremediation plan (Keller *et al.*, 2003).

Choice of crop is a management tool for polluted agricultural land (Hough *et al.*, 2003). For polluted impoldered soils, alternative crops such as leek, onion, potato and red cabbage may be grown instead of maize because metal uptake in these crops on a polluted sediment-derived soil was reported to be comparable to uptake on uncontaminated soils (Smilde *et al.*, 1982). Liming of the calcareous dredged sediment-derived soils is not an option. Hough *et al.* (2003) reported for a sewage sludge disposal site that metal concentrations in maize still exceeded legal standards after liming to adjust pH to 7.0. A more expensive management tool involves covering the soil with a non-polluted topsoil. However, for maize the required thickness varies between 0.2 and 1.2 m (van Driel *et al.*, 1995) because rooting depth is a function of groundwater level (van Noordwijk *et al.*, 1995). In a broader context, agricultural use of polluted soils is only acceptable after comprehensive risk assessment. Manuring (Lorenz *et al.*, 1994) polluted soils may result in a decreased pH and accordingly a higher bioavailability of heavy metals. Depending on the geometry of the area, metal transport from the sediment disposal site to surrounding areas by surface run-off may be of concern (Singh *et al.*, 2000). Effects of tillage practices and soil export at harvest are other factors to be considered in managing these contaminated soils. Drastic land use changes caused by tidal marsh restoration as a strategy for polluted impoldered marshes must be accompanied with ecological risk assessment, because elevated metal concentrations in the marsh vegetation may increase metal cycling.

Conclusions

In this study metal concentrations were measured in maize, willows and poplars growing on natural or impoldered freshwater tidal marshes (FTM) and on polluted sediment-derived soils. In general, normal to slightly elevated foliar Cd and Zn concentrations were found. Cd and Zn tended to be less available to willows on FTM than on polluted dredged sediment-derived soils. The data set is too limited for determining unambiguously whether the location in the estuary, the sampled species, the elevation of the tidal marsh or the Eh status of the soil affects the measured foliar concentrations. Willow and poplar leaves entering the biogeochemical cycle during autumn can be seen as a fertilizer application. Maximum allowable doses required by Flemish legislation were exceeded in 38% of the plots for Cd and 23% for Zn.

Choice of crop is a management tool for polluted agricultural land on impoldered FTM. In a broader context, agricultural use of polluted soils can only be accepted after comprehensive risk assessment, taking into account effects of manuring, surface run-off, tillage practices and soil export at harvest.

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