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SOME CHARACTERISTICS OF ORGANIC SOILS IRRIGATED WITH MUNICIPAL WASTEWATER

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ABSTRACT

Soil irrigation with wastewater (WW) gives the opportunity to solve the problems of its disposal, final purification or reuse. Many studies have examined mineral soils upon continued WW application. The aim of this paper was to examine the properties of organic soils 3 years after WW application was discontinued. Peat-muck soil planted with *Populus* spp. or *Salix* spp., and mineral-muck soil under grasses were irrigated for 4 years with municipal WW at a low (comparable with intensive NPK fertilization) and high WW rate (600 and 1200 mm yearly, respectively). Soils were analysed for organic matter (OM), pH, bulk density (BD), water holding capacity (WHC), P_2O_5, Fe_2O_3, Al_2O_3, MnO, Zn, Pb, Cu, Cr, magnetic susceptibility (MS) and dehydrogenase and catalase activities. The results were compared with control soils which have never received WW. The study showed that only P_2O_5, MnO and catalase activity (CA) were significantly affected by former WW application. On average, P_2O_5 increased by 30 per cent, whereas MnO decreased by 35 per cent with no differences between the two WW rates. CA decreased by 18 per cent at the high WW rate. Most of tested characteristics were determined by soil type. The peat-muck soil showed higher OM, WHC, P_2O_5, MnO, Pb and CA than mineral-muck soil and lower BD, MS, Fe_2O_3, Al_2O_3 and Cr. Soil depth influenced Fe_2O_3, MnO, Zn, MS and enzyme activities, while basic soil properties (OM, pH, BD, WHC and P_2O_5) were not changed by soil depth. Heavy metals (Zn, Cr, Cu and Pb) were below upper permissible limits. Copyright © 2010 John Wiley & Sons, Ltd.

KEY WORDS: Poland; organic soil; muck soil; municipal wastewater; soil properties; heavy metals; soil biochemical activity

INTRODUCTION

Soil irrigation with wastewater (WW) is a problem dating back to ancient times (Filip *et al*., 1999; Hoffmann *et al*., 2002; Hulugalle *et al*., 2006; Levy, in press). Globally, around 20 million ha of land are irrigated with WW. This is likely to increase markedly during the next few decades as water scarcity intensifies. The rationale for the practice tends to differ between the developing and developed world. In developing nations, the prime drivers are livelihood dependence and food security, whereas environmental agendas appear to hold greater sway in the developed world (Hamilton *et al*., 2007). In many European countries, including Poland, water exploitation rate exceeds 20 per cent of existing reserves, and water management becomes a vital element of the economy of the country (Angelakis *et al*., 2003). The reuse of treated WW could be an important option to shore up conventional resources and reduce the environmental impact of discharges, mainly related to an excessive or unbalanced supply of nutrients and the introduction of pollutants to ground water. The cultivation of inedible plants allows to combine these ecological and economical aspects of WW utilization. Poplars (*Populus* spp.) and willows (*Salix* spp.) are among most common tree species used for WW application sites (Kowalik and Randerson, 1994; Aronsson *et al*., 2002).

Although many studies have examined the impacts of WW on soil properties, they report the results under continued WW application, but the status of formerly irrigated fields – a period of time after WW application was stopped – has received relatively little attention. Such studies, however, may provide information on the persistence of the changes induced by WW in irrigated soil, both beneficial and unfavourable. Stopping the WW supply may induce a number of unfavourable soil processes as intensive mineralisation of organic matter (OM), acidification, mobilization of heavy metals and their transport to the groundwater (Hoffmann *et al*., 1999).

Light sandy and loamy-sandy soils which are permeable and show low water retention are considered to be most suitable and are used most frequently for WW treatment. Some field experiments with muck soils showed their effectiveness in the removal of excess nitrogen and phosphate from WW (Filipek, 1998; Kotowska *et al*.,

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2007). Muck soils, formed from peats during the secondary transformation, show lower water retainability than peats, but hold their high sorptive capacity (McKay *et al*., 1998; Sokołowska *et al*., 2000, 2004, 2009; Okruszko and Ilnicki, 2003). Field area covered with muck soils, which are of relatively poor quality as agricultural soils, could be useful in final WW treatment. The question remains how WW application alters organic soil, and whether discontinuation of this practice allows soil to recover or hold its original and enhanced properties.

The aim of this paper was to examine the properties of organic soils (peat-muck soil planted with *Populus* spp. or *Salix* spp., and mineral-muck soil covered with grasses) irrigated with secondary treated WW. The measurements of soil pH, bulk density (BD), water holding capacity (WHC), contents of OM, P_2O_5, Fe_2O_3, Al_2O_3, MnO, Zn, Pb, Cu, Cr, magnetic susceptibility (MS) and enzyme (dehydrogenase and catalase) activity were performed 3 years after 4-year WW application was discontinued. The results were compared with control soils which have never received WW. The effect of WW on soil properties was compared with these exerted by soil type and soil depth.

MATERIALS AND METHODS

Site Description and Soil Sampling

The study was conducted at Hajdów Research Station near Wastewater Treatment Plant of the city of Lublin (about 400 thousands inhabitants, south-east part of Poland). The 8-ha experimental field located in the valley of the Bystrzyca River was divided into seven plots and planted with different plants in 1997 (Filipek, 1998). Three plots were used to conduct this experiment: plot covered with poplar (*Populus nigra* and *P. alba*), willow (*Salix americana* and *S. viminalis*) and grasses (with domination of *Alopecurus pratensis*, *Phalaris arundinacea* and *Festuca pratensis*) (Figure 1). Each about 1-ha plot was divided into three subplots separated with dams (Control, Low WW and High WW). Control subplots were not irrigated and received only natural precipitation. The Low WW and High WW subplots were irrigated at low or high WW rates (60 or 120 mm, respectively), 10 times per year during vegetation seasons (April–October) over the four consecutive years (1997–2000). This means that Low WW and High WW subplots received yearly 600 and 1200 mm of WW, respectively. The average rainfall in this area is about 550 mm per year.

The soils of experimental field are post-bog soils developed from sedge peat: peat-muck soil in plots underneath poplar and willow, and mineral-muck soil under grasses (Terric Histosol and Histi-Mollic Gleysol, respectively). Before the experiment, the area was managed for several years as a meadow. Basic characteristics of control soils are listed in Table I.

The WW was obtained after two-step (mechanical and biological) treatment, and was characterized by parameters (the ranges in $g\,m^{-3}$): COD (chemical oxygen demand) 30·1–56·3; BOD_5 (biological oxygen demand) 8·3–22·6; N-NH_4^+ 1·0–7·1; N-NO_3^- 20·2–38·4; N_{tot} 22·3–43·6; P-PO_4^{3-} 3·1–6·8; P_{tot} 3·7–7·0; Na^+ 24·3–69·4; K^+ 11·8–27·7; Ca^{2+} 59·7–95·2; Mg^{2+} 12·6–19·7; SO_4^{2-} 43·6–116·3; Cl^- 67·8–121·6; Zn 0·018–0·800; Cu 0·006–0·198; Pb 0·007–0·096 and pH of 6·5–8·4. Periodical WW application at a low WW rate provided nutrients at concentrations comparable with intensive soil fertilization, about 180 kg N ha^{-1}, 30 kg P ha^{-1} and 110 kg K ha^{-1} yearly. The concentration of heavy metals met the standards for WW reuse, and resulted in metal loading rates of about 0·9 kg Zn ha^{-1}, 0·12 kg Pb ha^{-1}, 0·09 kg Cu ha^{-1} and 0·09 kg Cd ha^{-1} per year. For a high WW rate, these amounts were doubled (Filipek, 1998; Kotowski *et al*., 1999).

Soil was sampled in 2003, 3 years after the discontinuity of WW application, from the depths of 0–10, 10–30, 30–50 and 50–70 cm, at three random sites from each subplot. The

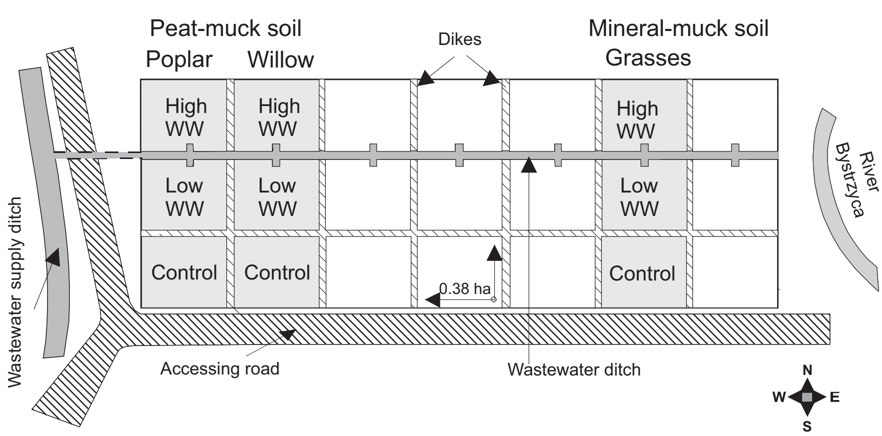

Figure 1. The scheme of the experimental site. Control – soil not irrigated with WW; Low WW – soil irrigated with the low wastewater rate, 600 mm per year; High WW – soil irrigated with the high wastewater rate, 1200 mm per year (after Brzezińska, 2006)

Table I. Basic characteristics of tested soils (after Brzezińska, 2006)

Soil–plant system	Soil depth (cm)	OM (%)	pH in $CaCl_2$	WHC (%, w/w)	BD ($Mg\,m^{-3}$)	P_2O_5 (%)
Peat-muck/poplar	0–10	30·3	7·93	174·3	0·515	0·442
	10–30	36·5	7·81	102·9	0·460	0·376
	30–50	47·9	8·92	227·0	0·307	0·623
	50–70	43·6	8·21	202·4	0·443	0·607
Peat-muck/willow	0–10	35·1	7·81	144·5	0·578	0·489
	10–30	41·1	7·80	128·5	0·627	0·473
	30–50	32·5	7·85	169·1	0·504	0·551
	50–70	42·6	8·56	385·6	0·375	1·69[a]
Mineral-muck/grasses	0–10	17·1	7·84	75·5	0·911	0·269
	10–30	24·6	7·63	65·3	0·976	0·246
	30–50	38·8	7·66	151·4	0·550	0·198
	50–70	31·0	7·76	63·8	1·042	0·151

OM, organic matter; WHC, water holding capacity; BD, bulk density.
[a]Not included in statistical analysis.

visible roots and mezofauna were removed and soil was sieved (4 mm). Biochemical parameters were determined in fresh soil, whereas physico-chemical in air-died soil. Additionally, undisturbed 100 cm^3 soil cores were collected from each subplot to determine soil BD and WHC.

Determination of Physico-Chemical Parameters and Enzyme Activities

Soil pH was measured in the 1:2·5 (v/v) suspensions of soil and 0·01 M $CaCl_2$. Soil OM was determined by the loss on ignition after ashing at 500°C for 2 h (Bauhus *et al*., 1998). BD was determined by gravimetric method from the proportion of the mass of soil dried at 105°C to volume of undisturbed soil core before drying (Witkowska-Walczak *et al*., 2002). WHC was calculated for undisturbed soil cores by the difference of water saturated and dry soil weight at 105°C (Singh *et al*., 2006).

Elemental concentrations in powder soil samples (P_2O_5, Fe_2O_3, Al_2O_3, MnO, Zn, Pb, Cu and Cr) were determined with the desktop XRF crystal diffraction scanning spectrometer SPECTROSCAN MAKC-GV® (Alekseeva *et al*., 1999). The quantitative analysis methods are based on the 12 standard soil calibration samples and then optimised using the computer simulation program. The MS of soils has been studied using the Kappabridge KLY-2 (Alekseev *et al*., 2002).

Soil dehydrogenase activity (DHA) was determined with triphenyltetrazolium chloride (TTC) according to Casida *et al*. (1964) and catalase activity (CA) by permanganate method of Johnson and Temple (1964). The measurements were done in triplicate and expressed on an oven-dry (105°C) weight basis.

Besides measured soil characteristics, both the sum of all measured metals (as elements) and heavy metals regarded as anthropogenic (Zn + Cr + Pb) for particular soils layers were calculated.

Statistical Analysis

Multi-factor analysis of variance (LSD test) was used to indicate which factors (soil–plant system, soil depth and WW treatment) significantly affect soil characteristics.

RESULTS

The distributions of measured properties in tested soils are presented in Figures 2–5. The results of analysis of variance with average values for particular soil–plant systems, soil depths and WW variants are listed in Tables II, III and IV, respectively.

Basic Soil Characteristics

Basic soil characteristics were differently distributed in tested soil–plant systems and experimental variants (Figure 2).

The OM varied within the range of 17·1 per cent and 48·3 per cent. Peat-muck soil under both plants showed significantly higher OM content than mineral-muck soil under grasses ($p < 0{\cdot}001$, Table II). The distribution of OM differed among experimental variants with no regular and no significant response to WW application.

The soils were alkaline, with pH (in $CaCl_2$) in the range of 7·15–8·92. Soil pH under poplar was much more variable and was significantly higher than under both willow and grasses ($p < 0{\cdot}001$, Table II). The effects of soil depth and WW application on soil pH were not significant (Tables III and IV, respectively).

BD ranged from 0·307 to 1·23 $Mg\,m^{-3}$ and WHC from 45·2 per cent to 386·5 per cent (w/w). Mineral-muck soil under grasses showed significantly higher BD but significantly lower WHC as compared with peat-muck soil under both plants ($p < 0{\cdot}001$). Neither BD nor WHC were affected by soil depth and WW application.

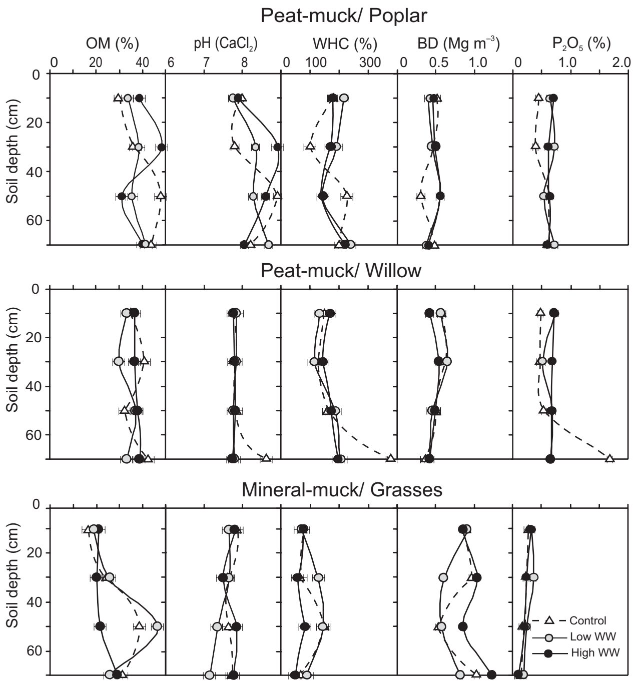

Figure 2. Distribution of organic matter (OM), pH, water holding capacity (WHC), bulk density (BD) and P_2O_5 in muck soils irrigated with municipal wastewater. Explanation as in Figure 1.

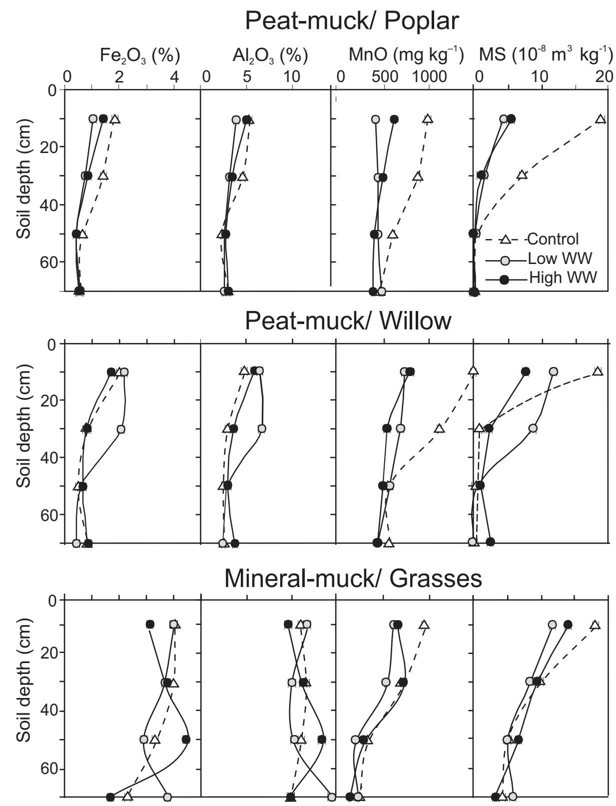

Figure 3. Distribution of the Fe_2O_3, Al_2O_3, MnO and magnetic susceptibility (MS) in muck soils irrigated with municipal wastewater. Explanation as in Figure 1.

The content of P_2O_5 varied between 0·104 per cent and 0·727 per cent. A high P_2O_5 value of 1·69 per cent in the deepest layer of control subplot under willow was not included in the statistical analysis. The P_2O_5 content in peat-muck soil under both plants was above 0·6 per cent, and was significantly higher than that in mineral-muck soil (0·24 per cent) ($p < 0{\cdot}001$, Table II). The changes with the depth were not significant (Table III). Soils irrigated with WW showed higher P_2O_5 content than control soils, by 32 per cent and 28 per cent for low and high WW rates, respectively ($p < 0{\cdot}01$, Table IV).

Metals Content in Soils

Figures 3 and 4 illustrate the distributions of measured metals. The Fe_2O_3 and Al_2O_3 contents varied between 0·44–4·43 per cent and 2·35–14·3 per cent, respectively, and MnO between 125 and 1503 $mg\,kg^{-1}$. The Fe_2O_3 and Al_2O_3 were more variable and about three times higher in mineral-muck soil under grasses than in peat-muck soil under both plants ($p < 0{\cdot}001$, Table II). The Fe_2O_3 significantly decreased with soil depth ($p < 0{\cdot}001$, Table III), while Al_2O_3 diminished slightly. No statistically significant differences among WW treatments for Fe_2O_3 and Al_2O_3 were observed (Table IV).

The MnO content was effected by all factors, namely, soil–plant system, soil depth and WW treatment. Peat-muck soil under willow showed the highest MnO (698·3 $mg\,kg^{-1}$) that was higher by 52 per cent than in mineral-muck soil under grasses (458·2 $mg\,kg^{-1}$, $p < 0{\cdot}01$, Table II). The MnO decreased with depth from 818 $mg\,kg^{-1}$ at 0–10 cm, till 376 $mg\,kg^{-1}$ at 50–70 cm ($p < 0{\cdot}001$, Table III) and decreased as the result of WW application, on average by 35 per cent (from 750·9 $mg\,kg^{-1}$ in control variant down to about 490 $mg\,kg^{-1}$ in irrigated variants ($p < 0{\cdot}001$, Table IV).

MS ranged from zero in deepest layer of peat-muck soil irrigated with the low WW rate, to 18·0–19·7 $\times 10^{-8}\,m^3\,kg^{-1}$ in surface layers of all control variants (Figure 3). The MS was significantly higher in mineral-muck soil under grasses than in peat-muck soil under both plants ($p < 0{\cdot}01$, Table II), and significantly decreased with depth ($p < 0{\cdot}001$, Table III). On average, the MS equalled to $7{\cdot}04 \times 10^{-8}\,m^3\,kg^{-1}$ in control soils, and 4·78 and $4{\cdot}37 \times 10^{-8}\,m^3\,kg^{-1}$ in soils irrigated at low and high WW rates, respectively. WW application apparently diminished the MS in surface layers (Figure 3), but differences among WW variants were not statistical significant (Table IV).

Heavy metals (Zn, Cr, Cu and Pb) in soil profiles are shown in Figure 4. The Cr was distributed most uniformly, especially in peat-muck soil. Conversely, Cu was most

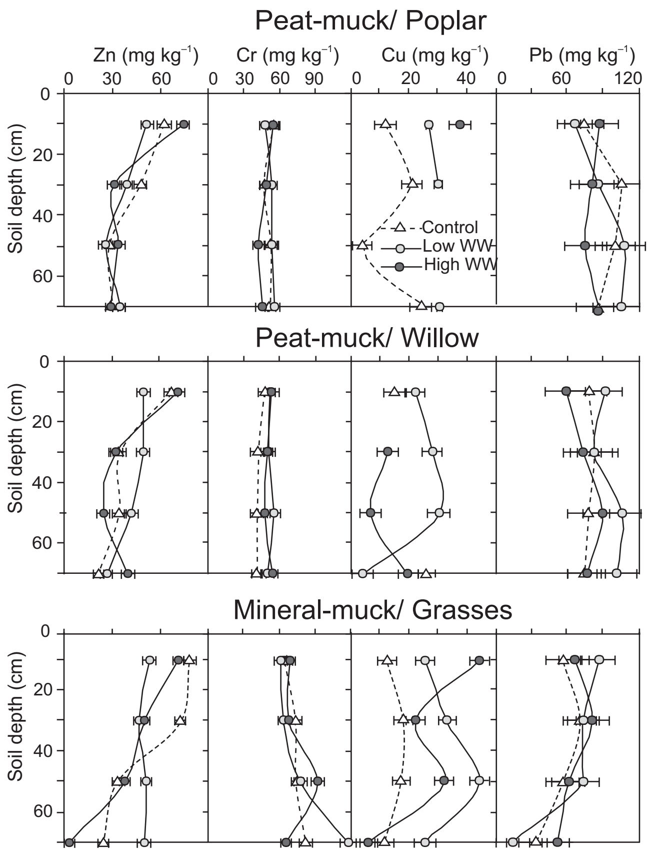

Figure 4. Distribution Zn, Cr, Cu and Pb in muck soils irrigated with municipal wastewater. Explanation as in Figure 1.

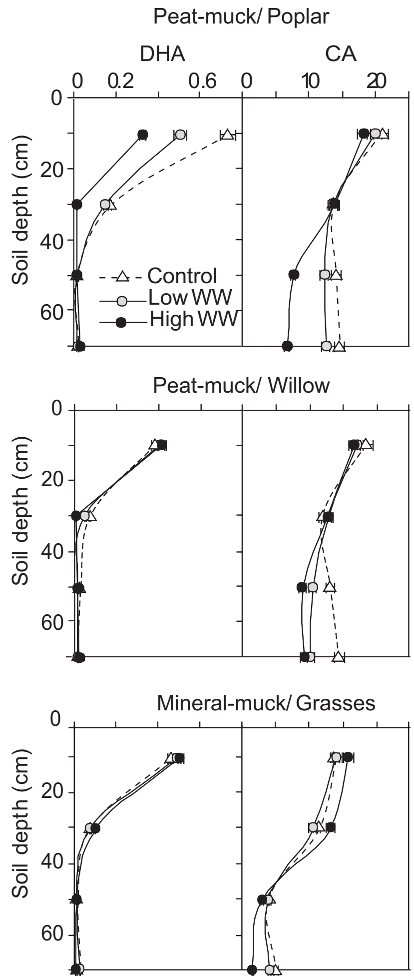

Figure 5. Distribution of dehydrogenase activity (DHA, nmol TPF g^{-1} min^{-1}) and catalase activity (CA, μmol H_2O_2 g^{-1} min^{-1}) in muck soils irrigated with municipal wastewater. Explanation as in Figure 1.

variable among variants and across the profiles. Because of the lack of some data for Cu, the results for this metal were not included in statistical analyses. The Cr and Pb contents were significantly influenced by soil–plant system (Table II). The Cr content was significantly lower in peat-muck soil (51·3 mg kg^{-1} under poplar, 49·0 mg kg^{-1} under willow) than in mineral-muck soil under grasses (76·1 mg kg^{-1}, $p < 0{\cdot}001$). On the contrary, the Pb content in peat-muck soil (on average 86 mg kg^{-1}) was significantly higher than that in mineral-muck soil (61·0 mg kg^{-1}, $p < 0{\cdot}001$). The Zn did not differ among soil–plant systems, while significantly decreased with depth, from 64·8 mg kg^{-1} at 0–10 cm, to 29·5 mg kg^{-1} at 50–70 cm ($p < 0{\cdot}001$, Table III). Heavy metals and calculated sum of Zn + Cr + Pb were not affected by WW treatment.

Soil Biochemical Activity

Soil biochemical activity in particular soil variants is presented in Figure 5. The DHA was not differentiated by soil–plant system, whereas CA was significantly higher in peat-muck soil (under both plants, on average 13·5 μmol H_2O_2 g^{-1} min^{-1}) than in mineral-muck soil (8·35 μmol H_2O_2 g^{-1} min^{-1}) ($p < 0{\cdot}001$, Table II). Both enzymes strongly decreased with depth ($p < 0{\cdot}001$, Table III). The effect of WW application on DHA was not significant. On the contrary, CA was significantly reduced by high WW application (by 18 per cent, $p < 0{\cdot}05$). The highest CA showed control soils (on average 12·9 μmol H_2O_2 g^{-1} min^{-1}) and the lowest showed soils irrigated with the high WW rate (10·6 μmol H_2O_2 g^{-1} min^{-1}) (Table IV).

DISCUSSION

The measurements performed 3 years after the end of WW application showed that among 16 tested soil properties only three (P_2O_5, MnO and CA) were significantly changed by a former WW irrigation practice. In turn, most of the measured properties have been shown to be influenced by soil type. Basic soil characteristics such as OM content,

Table II. Average values of tested soil properties for soil–plant systems used in the experiment

Soil characteristics	Soil–plant system			
	Peat-muck/poplar	Peat-muck/willow	Mineral-muck /grasses	Significance level
Organic matter (%)	38·8[a]	36·3[a]	26·7[b]	0·001
pH in $CaCl_2$	8·28[a]	7·86[b]	7·63[b]	0·001
Bulk density ($Mg\,m^{-3}$)	0·453[b]	0·506[b]	0·865[a]	0·001
WHC (%, w/w)	184·9[a]	180·2[a]	88·9[b]	0·001
P_2O_5 (%)	0·601[a]	0·615[a]	0·241[b]	0·001
Fe_2O_3 (%)	0·869[b]	1·19[b]	3·42[a]	0·001
Al_2O_3 (%)	3·44[b]	3·94[b]	11·1[a]	0·001
MnO ($mg\,kg^{-1}$)	577·4[a,b]	698·3[a]	458·2[b]	0·01
MS ($10^{-8} \times m^3\,kg^{-1}$)	3·27[b]	4·46[b]	8·52[a]	0·01
Sum of metals ($g\,kg^{-1}$)	24·9[b]	29·9[b]	83·2[a]	0·001
Zn ($mg\,kg^{-1}$)	41·2[a]	41·5[a]	48·0[a]	n.s.
Cr ($mg\,kg^{-1}$)	51·3[b]	49·0[b]	76·1[a]	0·001
Cu ($mg\,kg^{-1}$)	24·4	17·3	24·6	n.t.
Pb ($mg\,kg^{-1}$)	88·8[a]	82·8[a]	61·0[b]	0·001
(Zn + Cr + Pb) ($mg\,kg^{-1}$)	181·3[a]	173·3[a]	185·1[a]	n.s.
DHA (nmol TPF $g^{-1}\,min^{-1}$)	0·169[a]	0·120[a]	0·150[a]	n.s.
CA ($\mu mol\,H_2O_2\,g^{-1}\,min^{-1}$)	13·96[a]	12·97[a]	8·35[b]	0·001

WHC, water holding capacity; MS, magnetic susceptibility; DHA, dehydrogenase activity; CA, catalase activity; Sign., significance level; n.t., not tested; n.s., not significant.
Values within a row followed by the same letter do not differ significantly at $p < 0{\cdot}05$. Control – soil not irrigated, Low WW and High WW – soil irrigated with the low and the high wastewater rate (600 and 1200 mm per year, respectively).

WHC and BD were specific for muck soils, and were only affected by soil type, not by soil depth or WW application. The peat-muck soil showed significantly higher OM, WHC, P_2O_5, MnO, Pb and CA, while mineral-muck soil showed significantly higher BD, MS, Fe_2O_3, Al_2O_3, Cr and sum of all metals ($p < 0{\cdot}001$ and $p < 0{\cdot}01$ for MS and MnO).

Most organic soils have pH values ranging from 4·5 to 5·5 (Wright *et al*., 2009). In contrast, carbonate-muck horizons or organic soils which are neutral to alkaline in nature (pH 7–7·9) due to the underlying limestone (marl or shell) were observed by, for example, Qualls and Richardson (1995), Richardson and Vaithiyanathan (1995), Trąba and

Table III. Average values of tested soil properties for particular soil depth

Soil characteristics	Soil depth				
	0–10 cm	10–30 cm	30–50 cm	50–70 cm	Significance level
Organic matter (%)	29·4[a]	33·5[a]	36·6[a]	36·2[a]	n.s.
pH in $CaCl_2$	7·81[a]	7·92[a]	8·01[a]	7·97[a]	n.s.
WHC (%, w/w)	139·6[a]	124·4[a]	158·2[a]	183·2[a]	n.s.
Bulk density ($Mg\,m^{-3}$)	0·626[a]	0·650[a]	0·541[a]	0·615[a]	n.s.
P_2O_5 (%)	0·516[a]	0·473[a]	0·480[a]	0·474[a]	n.s.
Fe_2O_3 (%)	2·40[a]	2·03[a,b]	1·58[b,c]	1·30[c]	0·001
Al_2O_3 (%)	7·02[a]	6·33[a]	5·61[a]	5·66[a]	n.s.
MnO ($mg\,kg^{-1}$)	818·4[a]	685·5[a]	431·8[b]	376·3[b]	0·001
MS ($10^{-8}\,m^3\,kg^{-1}$)	12·4[a]	5·40[b]	1·99[c]	1·82[c]	0·001
Sum of metals ($g\,kg^{-1}$)	54·8[a]	48·5[a,b]	41·3[b]	39·6[b]	0·05
Zn ($mg\,kg^{-1}$)	64·8[a]	45·1[b]	34·9[b,c]	29·5[c]	0·001
Cr ($mg\,kg^{-1}$)	56·7[a]	55·7[a]	60·0[a]	62·8[a]	n.s.
Cu ($mg\,kg^{-1}$)	24·2	22·7	22·5	19·0	n.t.
Pb ($mg\,kg^{-1}$)	74·3[a]	82·1[a]	83·4[a]	70·2[a]	n.s.
(Zn + Cr + Pb) ($mg\,kg^{-1}$)	195·7[a]	183·0[a,b]	178·4[b]	162·6[b]	0·05
DHA (nmol TPF $g^{-1}\,min^{-1}$)	0·471[a]	0·081[b]	0·015[c]	0·018[c]	0·001
CA ($\mu mol\,H_2O_2\,g^{-1}\,min^{-1}$)	17·18[a]	12·60[b]	8·60[c]	8·67[c]	0·001

WHC, water holding capacity; MS, magnetic susceptibility; DHA, dehydrogenase activity; CA, catalase activity; Sign., significance level; n.t., not tested; n.s., not significant.
Explanation as in Table II.

Table IV. Average values of tested soil properties for wastewater variants used in the experiment

Soil characteristics	Wastewater application			
	Control	Low WW rate	High WW rate	Significance level
Organic matter (%)	35·1[a]	33·3[a]	33·4[a]	n.s.
pH in $CaCl_2$	7·98[a]	7·84[a]	7·96[a]	n.s.
WHC (%, w/w)	157·5[a]	156·3[a]	140·3[a]	n.s.
Bulk density ($Mg\,m^{-3}$)	0·607[a]	0·568[a]	0·649[a]	n.s.
P_2O_5 (%)	0·402[b]	0·529[a]	0·516[a]	0·01
Fe_2O_3 (%)	1·88[a]	1·89[a]	1·71[a]	n.s.
Al_2O_3 (%)	5·92[a]	6·38[a]	6·16[a]	n.s.
MnO ($mg\,kg^{-1}$)	750·9[a]	483·7[b]	499·3[b]	0·001
MS ($10^{-8} \times m^3\,kg^{-1}$)	7·04[a]	4·78[a]	4·37[a]	n.s.
Sum of metals ($g\,kg^{-1}$)	45·3[a]	47·6[a]	45·2[a]	n.s.
Zn ($mg\,kg^{-1}$)	45·2[a]	43·6[a]	42·0[a]	n.s.
Cr ($mg\,kg^{-1}$)	56·6[a]	61·9[a]	57·9[a]	n.s.
Cu ($mg\,kg^{-1}$)	15·4	27·8	23·1	n.t.
Pb ($mg\,kg^{-1}$)	74·9[a]	83·4[a]	74·2[a]	n.s.
(Zn + Cr + Pb) ($mg\,kg^{-1}$)	176·7[a]	188·9[a]	174·1[a]	n.s.
DHA (nmol TPF $g^{-1}\,min^{-1}$)	0·168[a]	0·148[a]	0·122[a]	n.s.
CA ($\mu mol\,H_2O_2\,g^{-1}\,min^{-1}$)	12·91[a]	11·78[a,b]	10·60[b]	0·05

WHC, water holding capacity; MS, magnetic susceptibility; DHA, dehydrogenase activity; CA, catalase activity; Sign., significance level; n.t., not tested; n.s., not significant.
Explanation as in Table II.

Wolański (2004), Niedźwiecki *et al*. (2009) and Wright *et al*. (2009). In our experiment, mineral-muck soil showed average pH 7·63, and peat-muck soil showed pH 7·80 and 8·29 (under willow and poplar, respectively).

WW application resulted in soil enrichment with P_2O_5 by about one-third when compared with controls, with no distinct difference between the two WW rates ($p < 0{\cdot}01$). This effect was more distinct in upper soil layers of peat-muck soil under both poplar and willow (Figure 2), and probably reflects the sorption of phosphate from WW during its percolation through the soil. Tested soils were previously found to show a high efficiency in PO_4^{3-} elimination (Kotowska *et al*., 2007). There are few data on the occurrence of Ca phosphate minerals (apatite and hydro-apatite) or other phosphates in soils; rather, it has been suggested that the intimate mixture of Ca, Fe and Al phosphates predominates in soils (Kabata-Pendias and Pendias, 2001). Basic soil conditions (pH >7·5) cause excessive calcium to be present in soil solution, which can precipitate with P, ultimately decreasing its availability to plants (Wright *et al*., 2009). Richardson and Vaithiyanathan (1995) observed that linear phosphate adsorption coefficient of the alkaline peat soils was higher than that of acidic bog peat soils, but lower than wetland soils and sediments with a high mineral content. Qualls and Richardson (1995) showed for the same peat soils (pH 7·2–7·9) that formation of Ca-bound P was an important mechanism of P deposition at the experimental stations closest to the phosphorus input from agricultural runoff. The increase of P level in mineral soil irrigated with treated WW was reported by Mohammad and Mazahren (2003).

The MnO was depleted in WW irrigated subplots, on average by 35 per cent. The effect of WW was even stronger than that of soil type ($p < 0{\cdot}001$ vs. $p < 0{\cdot}01$). As for P_2O_5, no significant difference between the two WW rates were found. The effect was more pronounced in peat-muck soil (under both plants) and in upper soil layers (Figure 3). Although soil components such as Fe/Al hydroxides and carbonates show high capacity to Mn sorption (in comparison with other metals), in organic soils Mn is relatively mobile because it is relatively weakly bound with soil OM (Kabata-Pendias and Pendias, 1999). In general, the sorption of Mn onto soils can be facilitated by several mechanisms: firstly, the oxidation of Mn to higher-valence oxides and/or precipitation of insoluble compounds in soils subjected to wetting and drying, secondly, absorption into the crystal lattice of clay minerals and adsorption on exchange sites (Bradl, 2004). In our experiment, the tested soils were subjected to wetting and drying due to the periodic WW application but showed low clay minerals content due to the properties of parent peat material. Appreciable depletion of available Mn in mineral soils irrigated with sewage for 5–20 years under intensive cultivation was observed by Rattan *et al*. (2005). On the contrary, Mohammad and Mazahren (2003) observed the increase in Mn level in mineral soils irrigated with treated WW.

The key to WW purification in soil–plant system is predictable water and nutrient uptake by plants. However, soil biochemical activity is equally important since a great number of reactions and processes in soil bio-filter are mediated by the microorganisms. Catalase and dehydrogenase enzymes belong to the same class of oxidoreductases but they play other roles in cell metabolism and differently respond to soil oxygen status (Gliński *et al.*, 1986; Brzezińska *et al.*, 1998). The catalase catalyses decomposition of hydrogen peroxide (H_2O_2) formed as a by-product during aerobic respiration. The function of catalase is essential for living cells because H_2O_2 creates the risk of irreversible damage of biomolecules (and is the price which aerobes have to pay for high efficiency of O_2-dependent respiration). The dehydrogenase enzymes are produced by all soil microorganisms (aerobic and anaerobic) and take part in the processes of bioavailable energy generation. Dehydrogenase and catalase activities belong to most frequently used biochemical indices in soil. The decrease in both of them is commonly regarded to be indication of soil degradation (Burns, 1978).

In our experiment with muck soils, soil CA was slightly diminished at low WW rate (by 9 per cent) and was significantly reduced at high WW rate (by 18 per cent when compared with controls, $p < 0{\cdot}05$). In turn, the DHA was not affected by WW application. The DHA followed nearly the same pattern in all experimental variants, especially in soils under willow and grasses (Figure 5). We previously showed for the same soils at the beginning of WW application (during two first years of irrigation) that both enzymes were significantly affected by WW, and, on average, a decrease in CA, while the increase in DHA was observed (Brzezińska *et al.*, 2001). Three years after the WW application has been discontinued, the effect of WW application persisted in the case of CA, thus reflecting unfavourable changes in the population of aerobic microorganisms as the result of periodic soil flooding. The stimulation of DHA, which was previously observed and which presumably resulted from periodic nutrients amendment, was not stable and the activity returned now to the level of control soils. In numerous studies on soils irrigated with WW, both stimulation and reduction of soil microbial activities were observed (e.g. Filip *et al.*, 1999; Speir, 2002).

Most of parameters relating to the content of metals have been found to be dependent on soil type and soil depth. Mineral-muck soil was characterized by higher MS and higher metal contents (except for MnO and Pb which were lower than in peat-muck soil). Most of these characteristics decreased with the soil depths, and only Al_2O_3, Cr and Pb were independent of the depth. However, as it was mentioned above, only MnO content was changed by WW application. In the experiments with mineral soils, Mohammad and Mazahren (2003) observed an increase in Fe and Mn levels and no significant effect for Cu and Zn as the result of irrigation with treated WW. Rusan *et al.* (2007) reported no significant effects for Pb and Cu, while the effects for Zn, Fe and Mn varied depending on soil depth and duration of WW application.

The content of Fe, Al and Mn elements in other muck soils of Poland range between: 0·54–3·87 per cent for Fe, 0·1–3·5 per cent for Al and 20–2200 mg kg^{-1} for Mn (Kabata-Pendias and Pendias, 1999; Malinowski, 2007; Mocek *et al.*, 2007). In our experiment, the Fe, Al and Mn expressed as elements showed maximum values of 3·1 per cent, 7·56 per cent and 1157 mg kg^{-1}, respectively. Thus, Mn was in the middle of its range, Fe was close to the highest value, while Al highly exceeded its range. The high Al and Fe levels in the tested muck soils may partly be responsible for the increase of P_2O_5 in WW irrigated subplots, as the accumulation of Al and Fe in organic soils increases their capacity of phosphate sorption (Giesler *et al.*, 2005; papers therein).

MS can provide rich environmental information, especially for hazardous heavy metals in the contaminated soils (Strzyszcz and Magiera, 1998; Yang *et al.*, 2009). In our experiment, WW application apparently altered the MS in surface layers (Figure 3), but this effect (on average diminish by one-third) was not significant. The MS in mineral-muck was twice as high as in peat-muck soil, and dropped with depth from in average $12{\cdot}4 \times 10^{-8}\,m^3\,kg^{-1}$ in surface layer down to $1{\cdot}82 \times 10^{-8}\,m^3\,kg^{-1}$ at the depth of 50–70 cm. Maximum MS values measured in tested muck soils ($18{\cdot}04 \times 10^{-8}$–$19{\cdot}7 \times 10^{-8}\,m^3\,kg^{-1}$) were much lower than MS values previously observed in mineral soils (5×10^{-8}–$30 \times 10^{-8}\,m^3\,kg^{-1}$ for brown soils and 15×10^{-8}–$70 \times 10^{-8}\,m^3\,kg^{-1}$ for degraded chernozem) (Alekseev *et al.*, 2002).

The contents of heavy metals in other organic soils of Poland vary within the ranges (in mg kg^{-1}), accordingly: Zn – 3·11–250·0; Cu – 1·0–110; Cr – 2·1–30·0 and Pb – 0·38–85·0 (Kabata-Pendias and Pendias, 1999; Malinowski, 2007; Mocek *et al.*, 2007). The contents of Zn and Cu in tested soils were relatively low, within the ranges of 3·74–78·7 and 4·03–44·4 mg kg^{-1}, respectively. In turn, the contents of Cr and Pb were relatively high, within the ranges of 41·1–117·6 mg kg^{-1} for Cr and 14·3–108·3 mg kg^{-1} for Pb. However, the highest concentrations were below the upper limits accepted by the European Union for heavy metals, namely, 300 mg kg^{-1} for Zn and Pb, and 140 mg kg^{-1} for Cu (CEC, 1986). Cr was below of 140 mg kg^{-1}, which is permissible for Cr in Poland (Directive, 2002).

Soil pH and OM content are important parameters controlling heavy metals adsorption and their distribution between soil and water. In general, greater metal retention and lower solubility occurs at high soil pH. Soil OM exhibits a large number and variety of functional groups and high cation exchange capacity values, which results in enhanced heavy metal retention ability mostly by surface complexation, ion exchange and surface precipitation (Bradl, 2004).

In our experiment with muck soils, no accumulation of heavy metals as the result of WW irrigation has been observed despite potentially high sorption capacity of muck soils and high soil pH. Anthropogenic heavy metals (Zn, Cr, Cu and Pb) were not accumulated even at the high WW rate. However, it is possible that heavy metals leached during WW application due to simultaneous introduction of dissolved organic compounds. Dissolved fraction of OM strongly influences sorption equilibra in soil by binding with heavy metals and leaching them as dissolved organics move through soil profile with soil water (Dube *et al*., 2001; Hoffmann *et al*., 2002).

CONCLUSIONS

The study performed on muck soils irrigated with WW has shown that tested soil properties were more strongly affected by inherent soil properties, that is, by soil type and soil depth, than by former 4-year WW application practice. Among 16 soil characteristics, only three were significantly changed by WW application. The P_2O_5 content increased by about 30 per cent ($p < 0{\cdot}01$), whereas MnO content decreased by about 35 per cent ($p < 0{\cdot}001$) when compared with the controls, with no distinct differences between two WW rates. The CA was reduced by about 18 per cent in soils irrigated with the high WW rate ($p < 0{\cdot}05$).

The parameters relating to the content of metals were in most cases determined by both soil type and soil depth and were not affected by WW application (except MnO). Mineral-muck soil was characterized by higher MS and content of Al_2O_3, Fe_2O_3, Cr, while lower MnO and Pb. Heavy metals (Zn, Cr, Cu and Pb) were below the upper permissible limits, even in soils irrigated at a high WW rate.

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