Biogeochemistry (2008) 88:117–126
DOI 10.1007/s10533-008-9198-3

ORIGINAL PAPER

From sediment to soil: floodplain phosphorus transformations at the Danube River

Franz Zehetner · Georg J. Lair · Franz-Josef Maringer · Martin H. Gerzabek · Thomas Hein

Received: 23 August 2007 / Accepted: 19 March 2008 / Published online: 18 April 2008

Abstract Substantial transformations of biogeochemical phosphorus (P) fractions can occur within a few hundreds of years under humid and tropical conditions; however, slower changes are expected under dry and temperate climate. The objective of this study was to infer P transformations over time by comparing suspended sediments in the Danube River to floodplain soils developed from such sediments over different time periods in the continental climate of Central Europe. We analyzed suspended sediments from 20 flood events between 1990 and 2006, and floodplain soils from seven sites along a chronosequence covering about 500 yrs. The studied flood sediments had similar characteristics over the 16-yr observation period. Total phosphorus (TP) averaged 732 mg kg^{-1}, and biogeochemical fractionation yielded important primary mineral contributions (apatite phosphorus, AP, $\sim$80% of TP). The TP concentrations of the floodplain soils were in the range of the Danube sediments and showed little variation along the chronosequence. However, the distribution of P among biogeochemical fractions changed considerably in less than 500 yrs of soil development. The youngest soils (<20 yrs) were dominated by AP, as was observed for the Danube sediments. In less than 250 yrs of pedogenesis, AP markedly decreased and organic phosphorus (OP) increased, and in less than 500 yrs, OP reached AP levels. This shows that while P biogeochemistry in very young floodplain soils is strongly related to the river sediments, significant transformations can occur in less than 250 yrs of soil development in the dry and temperate climate of Central Europe.

Keywords Chronosequence · Fluvisol · Pedogenesis · Phosphorus fractionation · Phosphorus transformation · Weathering index

Abbreviations

MAT	Mean annual temperature
MAP	Mean annual precipitation
MAPET	Mean annual potential evapotranspiration

Introduction

The transport of phosphorus (P) with river sediments is part of a global biogeochemical translocation process,

F. Zehetner · G. J. Lair (✉) · M. H. Gerzabek
Institute of Soil Research, University of Natural Resources and Applied Life Sciences,
Peter-Jordan-Str. 82, 1190 Vienna, Austria
e-mail: georg.lair@boku.ac.at

F.-J. Maringer
LLC-Laboratory Arsenal, University of Natural Resources and Applied Life Sciences, Faradaygasse 3, Objekt 214,
1030 Vienna, Austria

T. Hein
Institute of Hydrobiology and Aquatic Ecosystem Management, University of Natural Resources and Applied Life Sciences, Max-Emanuel-Str. 17,
1180 Vienna, Austria

connecting the P pool of terrestrial soils with that of ocean sediments. When river sediments are deposited on floodplains, some P (temporarily) escapes this global process and is returned to the terrestrial environment, once more exposed to the agents of weathering and soil formation. The biogeochemistry of P in river floodplains is influenced by the nature of the deposited sediments (e.g., their P concentrations and forms, the degree of pre-weathering) and by their alterations in the course of soil formation.

Walker and Syers (1976) devised a conceptual model describing P transformations as a function of soil development. According to this model, primary mineral P dominates in the early stages of pedogenesis and slowly dissolves with time. The released P is partly taken up by organisms, thus entering the organic pool, and partly sorbed onto surfaces of secondary minerals. With progressing soil development, the latter fraction gets incorporated into the structures of pedogenic oxides. The model further shows an asymptotic decline of total P toward a terminal steady state, at which time occluded and organic P prevail and losses from the system approximately equal gains (Walker and Syers 1976).

The Walker and Syers model was later supported by an extensive review of P fractionation studies that covered a wide range of soil orders representing different development stages (Cross and Schlesinger 1995). Likewise, Crews et al. (1995) found that soil P pools on a 4-million-yr chronosequence in Hawaii followed the model of Walker and Syers (1976). Primary mineral P comprised about 80% of total P contents at a 300-yr-old site, about 60% at a 2,100-yr-old site, and decreased to 1% after 20,000 yrs of pedogenesis. Organic P contents increased from the youngest site to a maximum after 150,000 yrs of soil development and then declined again. Occluded P contents increased steadily with soil age (Crews et al. 1995).

Other studies in humid and tropical environments found notable shifts in biogeochemical P fractions within a few hundreds of years. For example, Singleton and Lavkulich (1987) reported a decline of primary mineral P in the upper 10 cm of a sandy soil chronosequence on Vancouver Island from about 190 mg kg^{-1} at a 127-yr-old site to about 10 mg kg^{-1} at a 550-yr-old site. Schlesinger et al. (1998) studied the distribution of biogeochemical P fractions in soils developing on the pyroclastic material of the 1883 Krakatau eruption. After 110 yrs of soil development, they found most soil P still in the primary mineral (apatite) form; however, losses of apatite P from surface horizons were accompanied by marked accumulations of organic P.

To our knowledge, there are no studies available that determine P transformation rates under dry and temperate climate, for which we expect slower changes in P biogeochemistry compared to humid and tropical conditions. The objective of our study was therefore to quantify the transformations of biogeochemical P fractions under the continental climate of Central Europe. We studied suspended river sediments and floodplain soils sampled in a chronosequence scheme (Huggett 1998), i.e., along a substrate age gradient covering about 500 yrs, at the Danube River near Vienna, Austria.

Materials and methods

Soil and sediment sampling

We selected seven sampling sites along a chronosequence in the *Donau-Auen* National Park east of Vienna (Fig. 1; MAT ~ 9°C, MAP ~ 550 mm, MA-PET ~ 570 mm). For sites I, III, and VI, ages of <20 ± 5 yrs, <250 ± 30 yrs, and <500 ± 60 yrs, respectively, were determined for the upper 60 cm of the pedon using ^{137}Cs (site I) and optically stimulated luminescence (OSL) dating (sites III and VI, unpublished data). We estimated the approximate age of the remaining sites by grouping the ratios of oxalate- to dithionite-extractable Fe (Torrent et al. 1980; Table 1). Most of the studied soils classify as Fluvisols and show progressing development with age towards the Chernozem group (Table 1). The selected sampling sites represent different land use categories (forest, grassland, agriculture; Table 1). The forest plant communities are *Salicetum albae* (site I), *Salici-Populetum* (site III), and *Fraxino-Ulmetum* (site VI). The grassland plant communities are *Onobrychido viciifoliae-Brometum* (sites IV, V) and *Mesobrometum* (site VII). Site II is located in an agricultural field and was included to assess the impact of agricultural land use (mainly cereal production) on P biogeochemistry in the studied floodplain environment. Sites IV and V are located on grassland divided by a flood control dike that was constructed between 1882 and 1905 (Fig. 1).

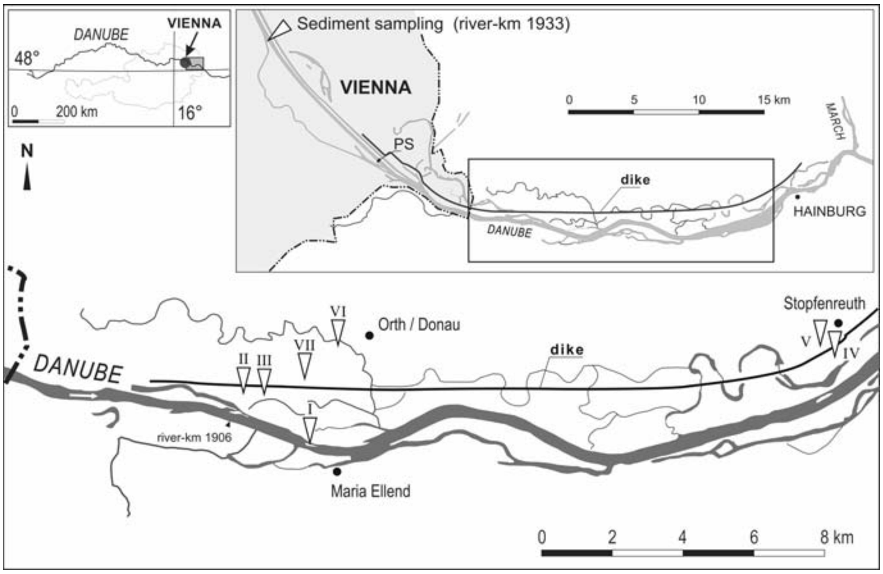

Fig. 1 Study area; ▽ = sampling sites (numbered I–VII), PS = run-of-river power station

At each site, we sampled two soil cores 15 m apart using a soil core sampler with 8 cm internal diameter. The core samples were divided into the depth increments 0–5 cm, 5–10 cm, and 10–20 cm from the soil surface. At the plowed site (site II), we took composite 0–20 cm soil cores, and at the island site (site I), we took additional samples in 10 cm intervals down to a depth of 60 cm for comparison with suspended sediments. Samples were air-dried and sieved (<2 mm).

We collected suspended sediment with a small-scale sediment trap at the right bank of Danube's main channel upstream of the studied floodplain (Fig. 1). Samples were retrieved from the sediment trap on a monthly basis, air-dried, and homogenized. For this study, we analyzed 20 sediment samples, each retrieved after a flood event in the period between 1990 and 2006 (Fig. 2, Table 2). The studied sediment record includes a 100-yr return event (Aug 15, 2002) with a peak discharge of more than five times the mean discharge.

Physicochemical analyses

Soil pH was measured in H_2O at a soil:solution ratio of 1:2.5 (Soil Survey Staff 2004). Total carbon was quantified by dry combustion (Tabatabai and Bremner 1991), and carbonate was measured gas-volumetrically (Soil Survey Staff 2004). Organic C was calculated as the difference of total and carbonate C. Particle size distribution was determined by wet-sieving (40–2,000 μm fraction) and sedimentation in a sedigraph (<40 μm fraction) after removal of organic matter with hydrogen peroxide and dispersion with sodium metaphosphate (Soil Survey Staff 2004). Iron associated with amorphous constituents (Fe_o) was extracted with acid ammonium oxalate using the method of Schwertmann (1964). Iron in (amorphous and crystalline) hydrous oxides (Fe_d) was estimated with the dithionite–citrate–bicarbonate method (Mehra and Jackson 1960). The extracted Fe was measured by atomic absorption spectroscopy.

Phosphorus fractionation was performed in duplicate according to the SMT protocol (Standards, Measurements and Testing Programme of the European Commission), which is based on the procedures proposed by Williams et al. (1976, 1980). The SMT protocol is described in Pardo et al. (2003), and consists of three extraction procedures, each applied to a 200 mg aliquot of finely ground soil or sediment. (1) One aliquot of the sample was extracted with 20 ml of 1 M NaOH for 16 h. A 10 ml aliquot of the supernatant was acidified with 4 ml of 3.5 M HCl to precipitate humic substances. After 16 h, *non-apatite inorganic P* (NAIP) was determined in the remaining supernatant. The residue of the NaOH extraction was extracted with 20 ml of 1 M HCl for 16 h, and calcium-associated *apatite P* (AP) was determined in the extract. (2) A second aliquot of the sample was extracted with 20 ml of 1 M HCl for 16 h, and the residue was placed in a porcelain crucible and

Table 1 Site description and topsoil (0–20 cm) characteristics in the studied Danube floodplain; estimated soil age using ^{137}Cs, OSL dating, and Fe_o/Fe_d ratios; coordinates according to WGS84, soil classification according to IUSS Working Group WRB (2006); all values are weighted averages of the sampling depths 0–5 cm, 5–10 cm, and 10–20 cm

Site	Coordinates		Site description	Soil classification	pH in H_2O	$CaCO_3$ ($g\ kg^{-1}$)	OC ($g\ kg^{-1}$)	BD ($g\ cm^{-3}$)	Clay ($g\ kg^{-1}$)	Sand ($g\ kg^{-1}$)	Fe_d ($g\ kg^{-1}$)	Fe_o/Fe_d	Soil age (yrs)
	East	North											
I a	16° 41′ 12″	48° 07′ 14″	Island, forest	Gleyic Fluvisol (Calcaric, Siltic)	7.26	215	10.8	1.15	140	320	3.8	0.84	<20
I b					7.34	203	7.7	1.10			3.0	0.77	<20
II a	16° 39′ 39″	48° 08′ 05″	Inside the dike, agricultural field	Gleyic Fluvisol (Calcaric, Humic, Siltic)	7.57	241	21.8	1.01	370	160	6.9	0.41	<250
II b					7.57	204	26.9	1.12			7.0	0.38	<250
III a	16° 39′ 47″	48° 08′ 03″	Inside the dike, forest	Gleyic Fluvisol (Calcaric, Humic, Siltic)	7.40	240	26.2	1.10	240	270	6.1	0.44	<250
III b					7.35	284	21.5	1.47			5.9	0.41	<250
IV a	16° 52′ 39″	48° 08′ 36″	Inside the dike, grassland	Gleyic Fluvisol (Calcaric, Humic, Siltic)	7.26	250	31.8	1.51	290	120	6.1	0.34	<250
IV b					7.36	273	29.6	1.45			6.2	0.38	<250
V a	16° 52′ 35″	48° 08′ 38″	Outside the dike, grassland	Gleyic Fluvisol (Calcaric, Humic, Siltic)	7.44	269	35.0	1.58	300	140	5.8	0.37	<250
V b					7.37	245	37.0	1.38			5.7	0.37	<250
VI a	16° 41′ 43″	48° 08′ 42″	Outside the dike, forest	Gleyic Fluvisol (Calcaric, Humic, Siltic)	7.62	244	28.4	1.00	360	160	6.7	0.32	<500
VI b					7.67	233	30.2	1.07			6.9	0.30	<500
VII a	16° 41′ 10″	48° 08′ 20″	Outside the dike, grassland	Endofluvic Calcic Chernozem (Siltic)	7.62	212	44.3	0.94	340	130	7.3	0.27	<500
VII b					7.70	203	42.1	1.10			7.1	0.27	<500

OC, organic carbon; BD, bulk density; Fe_d, dithionite-extractable iron; Fe_o, oxalate-extractable iron; Fe_o/Fe_d, weathering index

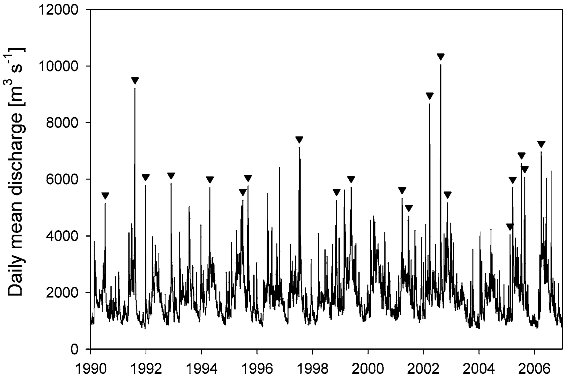

Fig. 2 Stream discharge hydrograph of the Danube River at Hainburg (river-km 1885) for the period between 1990 and 2006 (source: *via donau GmbH*); the 20 flood events included in this study are marked with triangles (▼)

calcined at 450°C for 3 h, then extracted again with 20 ml of 1 M HCl for 16 h to determine *organic P* (OP). (3) A third aliquot of the sample was extracted with 20 ml of 3.5 M HCl for 16 h after calcination at 450°C for 3 h, and *total P* (TP) was determined in the extract. In all extracts, phosphate was measured spectrophotometrically using the molybdenum blue method according to Murphy and Riley (1962).

Results and discussion

Basic characterization of suspended Danube flood sediments

The mean grain size distribution of the studied flood sediments was dominated by silt and sand-sized

Table 2 Characterization of suspended sediments from flood events between 1990 and 2006 in the Danube River

Date of flood peak	Daily mean discharge (m^3 s^{-1})	$CaCO_3$ (g kg^{-1})	OC (g kg^{-1})	Fe_d (g kg^{-1})	Fe_o/Fe_d	NAIP (mg kg^{-1})	AP (mg kg^{-1})	OP (mg kg^{-1})
Jul 11, 1990	5,148	193	4.4	5.1	0.55	81	594	89
Jul 29, 1991*	5,121	204	6.9	5.6	0.46	28	569	66
Aug 5, 1991*	9,214							
Dec 24, 1991	5,788	213	7.5	3.8	0.50	71	527	56
Nov 24, 1992	5,848	234	1.5	3.6	0.48	34	696	54
Apr 19, 1994	5,706	199	3.8	3.9	0.52	40	566	57
Jun 27, 1995	5,269	204	7.4	4.0	0.50	15	543	63
Sep 3, 1995	5,769	195	6.2	3.8	0.47	<10	612	51
Jul 9, 1997*	7,125	211	6.3	5.8	0.50	52	548	64
Jul 21, 1997*	6,713							
Nov 12, 1998	5,266	231	6.2	4.3	0.54	32	601	58
May 23, 1999	5,720	222	2.3	3.3	0.48	<10	728	40
Mar 25, 2001	5,330	200	6.9	3.5	0.60	42	655	45
Jun 20, 2001	4,706	268	14.9	5.8	0.59	38	569	97
Mar 23, 2002	8,669	208	4.9	3.6	0.61	103	597	85
Aug 9, 2002*	6,709	195	8.9	4.3	0.56	99	507	52
Aug 15, 2002*	10,055							
Nov 12, 2002	5,178	205	7.0	3.5	0.57	87	625	35
Feb 14, 2005	4,052	204	8.4	4.2	0.59	33	545	75
Mar 20, 2005	5,704	202	9.5	3.4	0.61	97	511	56
Jul 13, 2005	6,557	208	10.5	4.6	0.65	94	525	97
Aug 17, 2005*	4,571	219	7.2	4.7	0.55	14	547	63
Aug 25, 2005*	6,074							
Mar 30, 2006	6,967	195	10.6	5.0	0.68	151	552	98

*Composite sample analyzed

OC, organic carbon; Fe_d, dithionite-extractable iron; Fe_o, oxalate-extractable iron; Fe_o/Fe_d, weathering index; P fractionation according to Pardo et al. (2003): NAIP, non-apatite inorganic phosphorus; AP, apatite phosphorus; OP, organic phosphorus particles (500 g kg^{-1} and 440 g kg^{-1}, respectively) and characterized by low clay content (60 g kg^{-1}). Carbonate contents varied between 190 and 270 g kg^{-1} (Table 2), reflecting significant contributions from calcareous sources, such as the Northern Limestone Alps. The studied sediments had relatively low hydrous oxide-associated iron contents (Table 2; $\mathrm{Fe_d}$; mean, 4.3 ± 0.8 g kg^{-1}), which is characteristic of young and slightly weathered material. Likewise, organic carbon contents were low (Table 2; OC; mean, 7.1 ± 3.0 g kg^{-1}). Tockner et al. (1999) found organic portions of suspended solids in the Danube River near Vienna from 50 to 870 g kg^{-1} (mean, 240 g kg^{-1}). However, they noticed that the organic matter content of suspended solids was inversely related to water discharge. The low organic matter contents of the sediments in our study, which were collected during high discharge events, seem to confirm this trend.

Properties of floodplain soils along the chronosequence

The soils' particle size distribution was dominated by the silt fraction (Table 1), as was observed for the suspended Danube sediments. While the island soils (site I) had relatively low clay contents, soil textures were considerably finer on the floodplain (sites II–VII; Table 1). This is likely caused by decreasing flow velocity of flood water with increasing distance from the main channel, which allows finer particles to settle. The soils' carbonate contents match those of the Danube sediments and showed little variation across the chronosequence (Tables 1, 2). Likewise, soil pH varied in a narrow range above neutral (Table 1).

Organic carbon (OC) contents increased markedly from the island (site I, <20 yrs), where the values correspond with those of the Danube sediments, across the chronosequence, to the Chernozem (site VII, <500 yrs), which contained >40 g OC kg^{-1} (Table 1). This reflects the different duration of primary production and organic matter accumulation at the different sites of the studied chronosequence.

Iron associated with hydrous oxides ($\mathrm{Fe_d}$) was relatively low in the island soils (site I), corresponding with the Danube sediments, but was about twice as high in the soils on the floodplain (sites II–VII, Table 1). Hydrous Fe oxides have very small particle sizes (in the nm range) and are often associated with clay minerals (Kämpf et al. 2000). Therefore, the observed $\mathrm{Fe_d}$ distribution is likely related to differences in clay contents ($r = 0.90$, $p < 0.001$) and as such a result of different sedimentation conditions. In weakly developed soils, hydrous Fe oxides are generally dominated by amorphous forms, but progressing pedogenesis leads to increasing crystallinity. The ratio of amorphous to total hydrous Fe oxides ($\mathrm{Fe_o/Fe_d}$) is therefore an indicator of soil age and progressing pedogenesis (Schwertmann 1964; Torrent et al. 1980). In the studied soils, the $\mathrm{Fe_o/Fe_d}$ ratio decreased markedly from the island (site I), where amorphous Fe forms dominated, across the chronosequence, to the Chernozem (site VII), where about 75% of the hydrous oxide-associated Fe were crystalline (Table 1).

Phosphorus biogeochemistry in suspended Danube flood sediments

Total P in the studied flood sediments ranged from 619 to 846 mg kg^{-1}. This is considerably more than the TP concentrations reported by Teodoru and Wehrli (2005) for sediments in the Iron Gates Reservoir (Danube river-km 1045 to 944; TP range from 120 to 570 mg kg^{-1}) but less compared to sediments from the Danube Delta and Black Sea, where 1,090 and 950 mg kg^{-1}, respectively, were measured (Teodoru and Wehrli 2005). These differences in sediment quality likely reflect varying geological provenance and agricultural practices in different parts of the Danube catchment. The biogeochemical fractionation of sediment P yielded important primary mineral contributions (AP, ~80% of TP), and minor portions of P associated with hydrous oxides (NAIP) and organic matter (OP, Table 2). This points to relatively unweathered source materials (Walker and Syers 1976). However, mineral fertilizer P from agricultural runoff and P entering with urban waste waters could have contributed to the AP fraction in the studied sediments. Organic carbon was correlated positively with OP ($r = 0.51$, $p = 0.021$) and negatively with AP ($r = -0.64$, $p = 0.003$) in the suspended sediments. These relationships could indicate transformations of biogeochemical P fractions associated with allochthonous and/or autochthonous primary production.

No relations were found between peak discharge and sediment characteristics. The studied flood sediments had similar characteristics over the 16-yr observation period, and no temporal trends were discernible for most properties. The decreasing tendency in TP load (dissolved and particulate P) reported by van Gils et al. (2005) for the Danube River downstream of Vienna is not reflected by the TP concentrations in the studied sediments. The reason for this could be that during high flood events, fresh sediments entering from the catchment are mixed with older sediments remobilized from hydropower impoundments and groyne fields, thus masking any temporal trends.

Transformations of biogeochemical phosphorus fractions in floodplain soils

The studied floodplain soils had TP contents between 73 and 252 g m^{-2} in 0–20 cm depth (Table 3) and showed relatively high TP concentrations (mean, 713 ± 58 mg kg^{-1}), corresponding with those of the Danube sediments. This is in agreement with Cross and Schlesinger (1995), who found similar TP concentrations in weakly developed soils (Entisols, US soil taxonomy; Soil Survey Staff 2006). While the TP concentrations showed little variation across the chronosequence (data not shown), the distribution of P among biogeochemical fractions shifted markedly in the course of floodplain soil development (Fig. 3). The island soils (site I, <20 yrs) were strongly influenced by the river. Consequently, their P biogeochemistry corresponded with that of the suspended Danube sediments and was dominated by AP, with minor portions of NAIP and OP (Fig. 3). While NAIP remained at a low level throughout the chronosequence, AP and OP shifted markedly. In less than 250 yrs of soil development (sites II–V), AP markedly decreased and OP increased, and in less than 500 yrs (sites VI and VII), OP reached AP levels (Fig. 3). At the oldest sites of our study (sites VI and VII), land use seemed to have exerted additional influence on P transformation, with grassland (site VII) showing higher OP concentrations than forest (site VI; Table 3, Fig. 3).

The P biogeochemistry across the studied chronosequence was strongly affected by pedogenic development (Fig. 4). While AP was inversely related to an index of progressing weathering ($1 - Fe_o/Fe_d$), OP showed a strong positive correlation

Table 3 Total phosphorus (TP) contents and distribution of P among biogeochemical fractions in Danube floodplain soils; fractionation according to Pardo et al. (2003)

Site	0–20 cm TP (g m^{-2})	0–5 cm			5–10 cm			10–20 cm		
		NAIP (mg kg^{-1})	AP (mg kg^{-1})	OP (mg kg^{-1})	NAIP (mg kg^{-1})	AP (mg kg^{-1})	OP (mg kg^{-1})	NAIP (mg kg^{-1})	AP (mg kg^{-1})	OP (mg kg^{-1})
I a	160	76	615	42	67	678	32	71	638	56
I b	123	61	497	21	63	569	16	63	562	30
II a*	146	87	424	232	87	424	232	87	424	232
II b*	171	87	409	213	87	409	213	87	409	213
III a	191	113	472	147	85	402	207	55	374	201
III b	218	63	421	229	64	440	214	46	474	195
IV a	208	64	281	319	52	300	262	44	317	206
IV b	243	62	315	204	50	317	181	45	326	164
V a	252	82	334	275	57	313	249	44	455	244
V b	197	71	320	312	61	339	266	50	335	249
VI a	113	70	318	289	67	326	304	52	317	273
VI b	148	74	335	327	60	329	262	63	334	265
VII a	73	61	261	473	40	280	423	23	272	307
VII b	107	49	284	478	23	276	395	<10	289	272

*Soil homogenized by plowing

NAIP, non-apatite inorganic P; AP, apatite P; OP, organic P

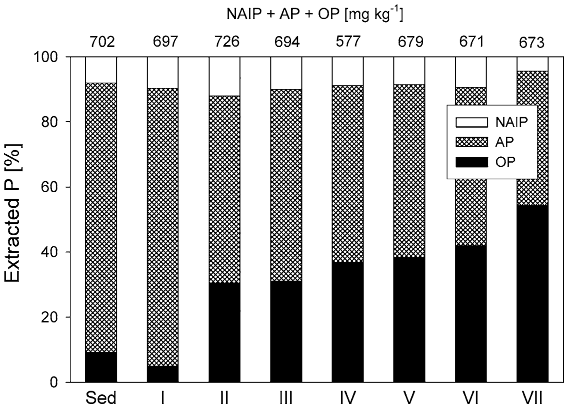

Fig. 3 Distribution of phosphorus (P) among biogeochemical fractions in Danube sediments and floodplain soils; P fractionation according to Pardo et al. (2003): NAIP = non-apatite inorganic P, AP = apatite P, OP = organic P; Sed: suspended sediments collected during flood events (1990–2006) in the Danube River (means of 20 samples); sites I–VII: weighted averages of the sampling depths 0–5 cm, 5–10 cm, and 10–20 cm of two replicate soil cores

(Fig. 4). At $1 - Fe_o/Fe_d \approx 0.65$, the amounts of OP started to overlap with those of AP. The Danube sediments showed characteristics indicative of young and slightly weathered material over the 16-yr record, and took a congruous place among the soil chronosequence samples in Fig. 4.

The sum of the fractions NAIP, AP, and OP was generally close to 100% of the TP concentrations, except for the oldest sites VI and VII, where only 87 and 86% of TP, respectively, were extracted in these fractions (data not shown). The remaining portion could be P occluded in the interior of hydrous oxide structures not extractable with 1 M NaOH; indeed, this portion was significantly correlated with Fe in crystalline hydrous oxides ($Fe_d - Fe_o$; $r = 0.70$, $p < 0.001$). The formation of an occluded P fraction seems therefore noticeable in the oldest soils (sites VI and VII, <500 yrs) of the studied floodplain chronosequence, which is consistent with the Walker and Syers model of P transformations.

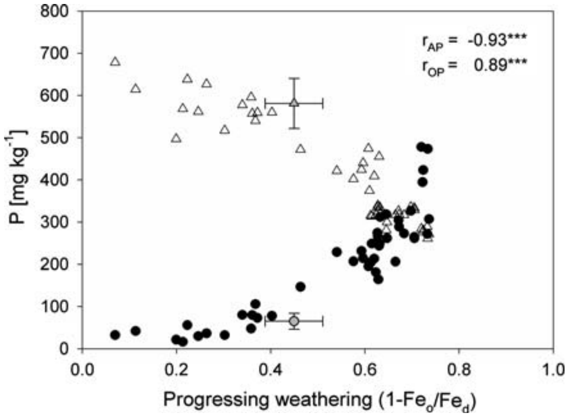

Fig. 4 Variations of apatite phosphorus (AP, △) and organic phosphorus (OP, ●) along a gradient of chemical weathering in the studied floodplain soils; $n = 46$, *** = significant at the 0.001 level; Danube sediments (grey symbols; means ± standard deviation) included for comparison

The biogeochemical P fractions in an agricultural field (site II) were comparable to those observed in an adjacent forest with similar sedimentation history (site III; Fig. 3). Evidently, the natural biogeochemical equilibrium has not been altered significantly through agricultural activities at site II. Likewise, biogeochemical P fractions were similar at sites IV and V (Fig. 3), which had been separated by a flood control dike about 100 yrs ago. This shows that recent inundation had minor impacts on P biogeochemistry at site IV.

The island soils (site I, <20 yrs) showed no consistent depth differentiation of biogeochemical P fractions (Table 3), which reflects lacking pedogenesis caused by regular disturbance through the river. With vegetation development and growth, organic matter and nutrients are expected to accumulate near the soil surface. For example, Richter et al. (2006) found an average net P transfer from mineral soil to plant biomass and O-horizons in an aggrading pine forest in the Southeastern US of 82.5 kg ha^{-1} over 28 yrs. In the soils on the Danube floodplain, both OP and NAIP tended to increase towards the soil surface (sites III–VII; Table 3), which is likely related to pedogenic development resulting in accretion of organic matter and amorphous hydrous oxides. This is supported by significant correlations of OP with OC ($r = 0.88$, $p < 0.001$) and NAIP with Fe_o ($r = 0.57$, $p < 0.001$).

The sedimentation conditions in the studied environment favored the deposition of coarse material on the island (site I) and finer particles on the floodplain (sites II–VII). The latter could have promoted the accumulation of OP through physical protection of soil organic matter (Hassink 1995). This is corroborated by significant positive correlations ($p < 0.001$) of OP with the particle size fractions <2 μm, 2–6.3 μm, and 6.3–20 μm ($r = 0.76$, 0.77, and 0.72, respectively) and significant negative correlations ($p < 0.001$) with the fractions 20–63 μm and 63–200 μm ($r = -0.78$ and -0.68, respectively). The

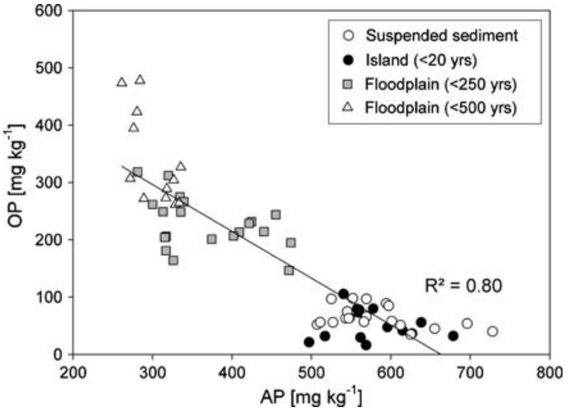

Fig. 5 Transformation of apatite phosphorus (AP) to organic phosphorus (OP) in the course of floodplain soil development; $n = 66$, $p < 0.001$

observed positive correlation of OP with the coarse sand fraction (630–2,000 μm; $r = 0.66$, $p < 0.001$) points to P bound in particulate organic matter.

In summary, the P transformations in the studied floodplain environment are consistent with the conceptual model of Walker and Syers (1976). The Danube sediments and island soils (site I, <20 yrs) are at the beginning of the transformation; sites II–V (<250 yrs) represent an intermediate stage with already significant amounts of OP; and at sites VI and VII (<500 yrs), the loss of AP and concomitant gain of OP has progressed farthest (Fig. 5).

Our study shows that the P biogeochemistry in very young floodplain soils is strongly related to the river sediments; however, significant transformations can occur in less than 250 yrs of soil development in the dry and temperate climate of the study area, i.e., similarly rapidly as reported for the tropical conditions of Krakatau (Schlesinger et al. 1998).

Acknowledgments This work was supported by the Danube Regional Project Component 4.3 funded by UNDP/GEF. Additional support came from the European Union FP6 Integrated Project AquaTerra under the thematic priority "sustainable development, global change and ecosystems" (Project no. GOCE 505428). We are grateful to *via donau GmbH* and *Nationalpark Donau-Auen GmbH* (Dr. Christian Baumgartner) for the fruitful cooperation.

References

Crews TE, Kitayama K, Fownes JH, Riley RH, Herbert DA, Mueller-Dombois D, Vitousek PM (1995) Changes in soil phosphorus fractions and ecosystem dynamics across a long chronosequence in Hawaii. Ecology 76:1407–1424

Cross AF, Schlesinger WH (1995) A literature review and evaluation of the Hedley fractionation: applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. Geoderma 64:197–214

Hassink J (1995) Density fractions of soil macroorganic matter and microbial biomass as predictors of C and N mineralization. Soil Biol Biochem 27:1099–1108

Huggett RJ (1998) Soil chronosequences, soil development, and soil evolution: a critical review. Catena 32:155–172

IUSS Working Group WRB (2006) World reference base for soil resources 2006. World soil resources rep 103. FAO, Rome

Kämpf N, Scheinost AC, Schulze DG (2000) Oxide minerals. In: Sumner ME (ed) Handbook of soil science. CRC Press, Boca Raton, FL, pp F125–F168

Mehra OP, Jackson ML (1960) Iron oxide removal from soils and clays by dithionite-citrate systems buffered with sodium bicarbonate. Clay Clay Min 7:317–327

Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal Chim Acta 27:31–36

Pardo P, López-Sánchez JF, Rauret G (2003) Relationships between phosphorus fractionation and major components in sediments using the SMT harmonised extraction procedure. Anal Bioanal Chem 376:248–254

Richter DD, Allen HL, Li J, Markewitz D, Raikes J (2006) Bioavailability of slowly cycling soil phosphorus: major restructuring of soil P fractions over four decades in an aggrading forest. Oecologia 150:259–271

Schlesinger WH, Bruijnzeel LA, Bush MB, Klein EM, Mace KA, Raikes JA, Whittaker RJ (1998) The biogeochemistry of phosphorus after the first century of soil development on Rakata Island, Krakatau, Indonesia. Biogeochemistry 40:37–55

Schwertmann U (1964) Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung. Z Pflanzenernaehr Dueng Bodenkd 105:194–202

Singleton GA, Lavkulich LM (1987) Phosphorus transformations in a soil chronosequence, Vancouver Island, British Columbia. Can J Soil Sci 67:787–793

Soil Survey Staff (2004) Soil survey laboratory methods manual. Soil survey investigations rep 42. USDA – NRCS, Washington, DC

Soil Survey Staff (2006) Keys to soil taxonomy, 10th edn. USDA – NRCS, Washington, DC

Tabatabai MA, Bremner JM (1991) Automated instruments for determination of total carbon, nitrogen, and sulfur in soils by combustion techniques. In: Smith KA (ed) Soil analysis. Marcel Dekker, New York, pp 261–286

Teodoru C, Wehrli B (2005) Retention of sediments and nutrients in the Iron Gate I Reservoir on the Danube River. Biogeochemistry 76:539–565

Tockner K, Pennetzdorfer D, Reiner N, Schiemer F, Ward JV (1999) Hydrological connectivity, and the exchange of organic matter and nutrients in a dynamic river-floodplain system (Danube, Austria). Freshw Biol 41:521–535

Torrent J, Schwertmann U, Schulze DG (1980) Iron oxide mineralogy of some soils of two river terrace sequences in Spain. Geoderma 23:191–208 van Gils J, Behrendt H, Constantinescu A, Laszlo F, Popescu L (2005) Changes of the nutrient loads of the Danube since the late eighties: an analysis based on long term changes along the whole Danube River and its main tributaries. Water Sci Technol 51:205–212

Walker TW, Syers JK (1976) The fate of phosphorus during pedogenesis. Geoderma 15:1–19

Williams JDH, Jaquet JM, Thomas RL (1976) Forms of phosphorus in the surficial sediments of Lake Erie. J Fish Res Bd Can 33:413–429

Williams JDH, Mayer T, Nriagu JO (1980) Extractability of phosphorus from phosphate minerals common in soils and sediments. Soil Sci Soc Am J 44:462–465