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Adsorption properties of modified natural materials for the removal of perfluorochemicals in AFFF wastewater

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Abstract
Perfluorooctane sulfonate (PFOS) pollution in water and soil environment is a global problem of concern. Naturally occurring materials have been prepared by a novel two step modification method. The material has been named as MatCARE™ (Patent Pending). The sorption behaviour of MatCARE™ was investigated using batch experiments with technical grade Ansulite (New Aqueous Film Forming Foam product) and AFFF wastewater. Results showed that MatCARE™ had good selectivity for fluorinated surfactants (PFOS & Perfluoro octanoicacid) with no influence of other organics and ions present in the AFFF wastewater.

Key Words
Natural materials, modification, wastewater, perfluorochemicals, PFOS and PFOA.

Introduction
Fire suppression systems using AFFF solutions are often installed in facilities containing flammable or combustible liquids because of the rapid and efficient fire extinguishing capability of foam. Within the Department of Defence, the primary application of AFFF fire suppression systems is in the facilities housing fuelled aircraft. Although various types of fire fighting foams are available, AFFF is used almost exclusively because of its superior fire extinguishing capacity. AFFF formulations contain a class of chemicals known as perfluorochemicals (PFC) namely PFOS and PFOA. PFC’s are very stable chemicals that do not change or break down in the environment, or in living things. As a result, they may be found in soil, sediments, water or in other places. When spilled or disposed of, PFC’s can enter groundwater and easily move long distances, potentially affecting nearby water supplies. All the constituents resulting from fire fighting exercises are considered to have adverse environmental effects. The organic constituents in the AFFF have been reported to resist biodegradation in conventional biological processes as well as contributing to operational problems. Industrial wastewater has been implicated as a likely prime source of entry of PFOS and PFOA into natural waters thereby entering domestic water (Schultz *et al.* 2006). Research efforts; therefore have been directed towards developing a remediation method for treating AFFF wastewater containing PFC’s.

Naturally occurring materials have found many applications as adsorbents. The capacity of such materials for the removal of contaminants can be greatly improved by mineral tailoring. Application of tailored materials offers several advantages, including; low cost of natural materials, versatility in the preparation of selective and modified materials for target contaminants and availability in abundance. Current work focussed on preparing and developing an efficient natural material-based adsorbent (MatCARE™).

Methods
The fire suppression foam products, 3% and 6% (Ansulite AFFF and AFFF wastewater) were supplied by the Department of Defence. All other chemicals (analytical standards of PFOS, PFOA) used in this investigation were purchased from Sigma-Aldrich Ltd. unless otherwise stated. The natural materials were obtained locally in Australia. Zeolites and MatCARE™ were utilised in the study.

Experimental procedures
Two types of experimental set up have been used to study the adsorption of 3% Ansulite and AFFF wastewater in the laboratory.

Batch Studies
The adsorption of AFFF technical grades Ansulite (3%) to MatCARE™ (Kambala *et.al*. 2009) was tested in triplicate by the addition of 20 ml of the usable concentration in various amounts of a sorbent in a 50 ml

tube. These tubes were rotated for twenty-four hours, centrifuged, filtered and then subjected to analysis by the methylene blue active substances (MBAS) assay to deduce the amount of usable concentration absorbed.

Analytical methods for detection of AFFF components in water

a) Qualitative Analysis

The MBAS assay is used to qualitatively determine the amount of methylene blue active substances in a sample by producing a measurable colour change in a separate solvent phase. At acidic pH (pH 2.4) negatively charged anionic detergents bind methylene blue, becoming hydrophobic and migrating into a lower chloroform solvent phase producing a colour change. The higher the concentration of anionic detergents present in a sample, the greater the colour change produced.

b) Quantitative Analysis

Mass spectral detection of the chemical components in AFFF products was achieved with an Agilent 1100 series LC/MSD (Agilent Technologies, USA). A diode array detection (DAD) system was connected in-line with an electron spray ionisation (ESI) interface. LC separation of surfactants (key ingredients of AFFF) was carried out with a Zorbax C8 column (C8, 5 µm, 150×4.6 mm, Agilent Technologies, USA).

Results

Effect of adsorbent dosage in batch studies

In the batch study it is essential to find the optimum adsorbent dose of the modified natural material and also contact time for maximum removal of contaminants. A series of 20 ml samples of Ansulite and AFFF wastewater were shaken for 2-20 hrs with adsorbent doses ranging from 0.5-1g. The initial concentrations of technical grade ansulite were made up of 3% solutions (97ml water and 3 ml Ansulite). It has been observed that the removal of ansulite increased with the increase in adsorbent dosage as shown in Figure 1. The removal of ansulite at an adsorbent dosage of 1g was found to be 96%. Hence, 1g was selected as the best dosage of adsorbent. The removal efficiency of AFFF wastewater is presented in figure 2. It is clearly shown that the dose of adsorbent and time was significantly less for 99% removal of contaminants in AFFF wastewater.

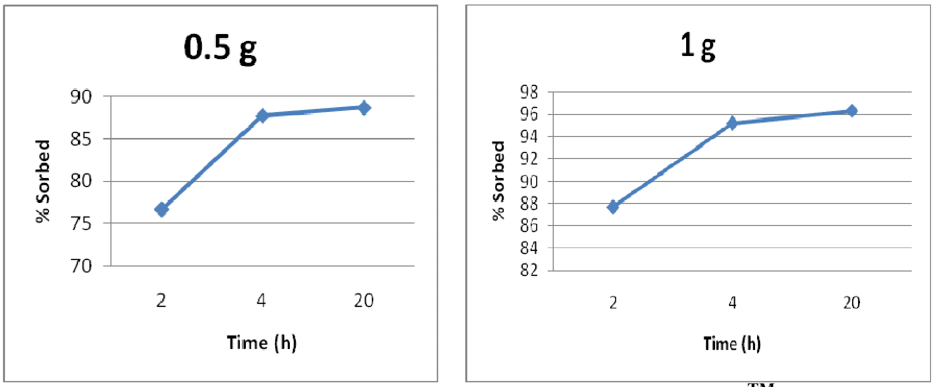

Figure 1. The removal efficiency of Ansulite (3%) using MatCARE^{TM}.

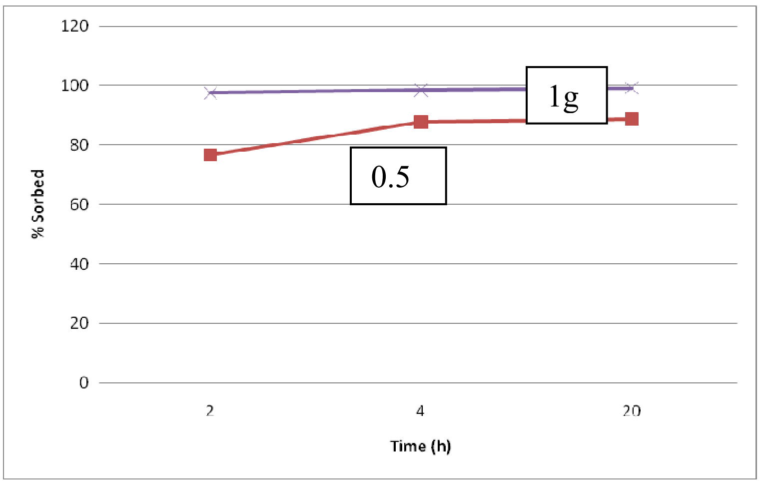

Figure 2. The removal efficiency of AFFF wastewater using MatCARE^{TM}

Conclusion

Modified natural materials can be used for the remediation of Ansulite and AFFF wastewater. In a batch study the optimum adsorbent dosage and equilibrium time for Ansulite was found to be 1g and 20 h respectively. In the case of AFFF wastewater the optimum dose was between 0.5-1g with an equilibrium time of 2h. Under optimised conditions, 96% of Ansulite and 98% of AFFF wastewater could be remediated using MatCARE™. Column in series design could be used for better performance of MatCARE™. After exhaustion of the modified material it could be used for the removal of other organic pollutants like dyes etc. from the wastewater, or it could efficiently be regenerated by subjecting it to different treatments for its further use with a fresh lot of AFFF wastewater. Pilot scale remediation trials are in progress to treat large volumes of AFFF wastewater.

Acknowledgments

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Evaluation of constructed wetlands for treating hydroponic waste solution containing high nitrate from greenhouses in South Korea

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Abstract
To treat the hydroponic waste solution containing high nitrate in constructed wetlands (CWs), the optimum conditions of *Thiobacillus denitrificans* (sulfur oxidizing denitrifying bacteria) were investigated in batch experiments under various conditions (amount of sulfur, the ratios of sulfur to calcite, and temperatures). For treating the hydroponic waste solution using *Thiobacillus denitrificans*, the optimum conditions were 3:1 for the ratio of sulfur to calcite and 30℃ for temperature in the study. To obtain optimum configuration, depth and loading of CWs for treating of hydroponic waste solution (HWS) which was produced in greenhouses, the study was conducted with four kinds of combined systems such as Vertical flow (VF)-Horizontal flow (HF), VF-VF, HF-VF and HF-HF CWs. In four configurations of CWs, the treatment efficiency of pollutants (COD, SS, T-N and T-P) under HWS loading and various HWSs were investigated. The optimum HWS loading was 300 L/m^2/d in four configurations of CWs. Depending on the optimum HWS lading, removal rate of COD, SS, T-N and T-P in HF-HF CWs was higher than that in HF-VF CWs under various HWSs (from cucumber, paprika and strawberry cultivation). Optimum configuration of 2-stage hybrid CWs was HF-HF CWs for treating hydroponic waste solution in greenhouses. Therefore, under the optimum conditions, removal rate of COD, SS, T-P, T-N and NO_3-N in HF-HF CWs were 53, 91, 91, 69 and 71%, respectively. Removal rate of nitrate in CWs with sulfur oxidizing denitrifying bacteria was higher than that in CWs without sulfur oxidizing denitrifying bacteria.

Key Words
Constructed wetlands, hydroponic waste solution (HWS), greenhouses, sulfur oxidizing denitrifying Bacteria (*Thiobacillus denitrificans*).

Introduction
Constructed wetlands are low-cost alternatives for treating municipal, industrial and agricultural wastewater. Over the last two decades, several studies have reported the potential use of wetlands for removal of nutrients, including nitrogen (N) and phosphorus (P) from wastewater (Reddy and Smith 1987; Mitsch and Cronk 1992). The objective of the study was to evaluate the constructed wetlands for treating hydroponic waste solution containing high nitrate from greenhouses in South Korea.

Methods
The small-scale hybrid constructed wetlands (located in Gyeongsang National University, South Korea at 35°16’N latitude and 127°56’E longitude) evaluated in the study consisted of 2-stage beds containing filter media (coarse sand, broken stone, and mixed filter media). The 2-stage hybrid CWS was conducted with 4 kinds of combined systems such as Vertical flow (VF)-Horizontal flow (HF), VF-VF, HF-VF and HF-HF CWs. The VF bed was 0.5 m (width) × 0.5 m (length) × 1.0 m (height) for the VF bed (0.25 m^3 total volume). The HF bed was 0.7 m (width) × 0.35 m (length) × 1.0 m (height) for the HF bed (0.25 m^3 total volume). In the VF bed, a ventilation pipe was installed at the bottom at 0.5 m in order to maintain natural ventilation. The HF bed was divided into four sections to maximize the hydraulic retention time in the bed.

Results
Optimum HWS loading and configuration of 2-stage hybrid CWs was 300 L/m^2/d and HF-HF CWs for treating hydroponic waste solution in greenhouses, respectively. Under optimum conditions, removal rates of COD, SS, T-P, T-N and NO_3-N in HF-HF CWs with *Thiobacillus denitrificans* was 53%, 91%, 91%, 69% and 71%, respectively. In control, the removal rates of COD, SS, T-P, T-N and NO_3-N in HF-HF CWs without *Thiobacillus denitrificans* was 55%, 93%, 93%, 51% and 47%, respectively.

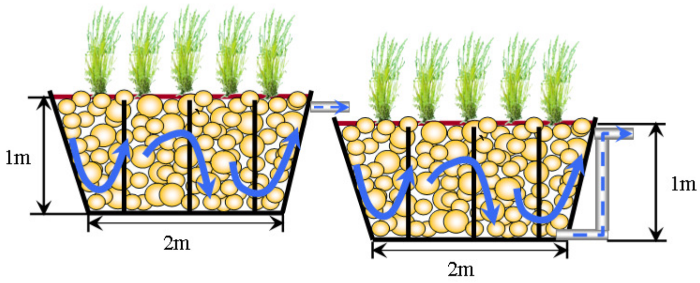

Figure 1. Diagrams of small-scale hydroponic waste solution treatment plant.

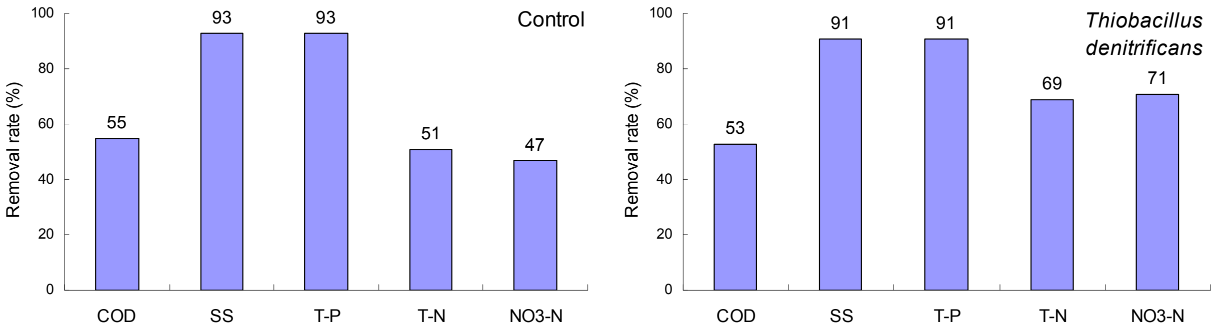

Figure 2. Removal rates of COD, SS, T-N T-P and NO_3-N the effluent under conditions of *Thiobacillus denitrificans* in HF-HF hybrid CWs.

Conclusion

In batch experiment, the optimum conditions were 3:1 for the ratio of sulfur to calcite and 30℃ for temperature in this study for treating the hydroponic waste solution containing high nitrate using *Thiobacillus denitrificans*. The optimum HWS loading was 300 Lm^2/d in four configurations of CWs. In addition, optimum configuration of 2-stage hybrid CWs was HF-HF CWs for treating hydroponic waste solution from greenhouses in CWs. Depend on optimum conditions, the removal rates of COD, SS, T-P, T-N and NO_3-N in HF-HF CWs with *Thiobacillus denitrificans* was 53%, 91%, 91%, 69% and 71%, respectively.

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Flow hydraulic characteristics and interrill erosion susceptibility of natural and constructed Soils from Candiota coal mining Area, RS, Brazil

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Abstract
Soil particles detachment in interrill soil erosion is due to water raindrop impact on the soil surface. The transport of soil particles is by overland broad sheet flow enhanced by the flow turbulence caused by raindrop impact. The objectives of this study were to evaluate the flow hydraulic characteristics, to determine detachment rate and the interrill soil erodibility factor under simulated rainfall under laboratory conditions. Soil samples from natural and from 12 years old constructed soil were taken from the 20 cm topsoil Candiota coal mine, RS, Brazil. Laboratory simulated rainfall of 85 mm/h intensity was applied during 90 minutes on bare soil at interrill unit plot of 0.59 x 0.59 m settled on 0.09 m/m slope. The results showed that the flow hydraulic was laminar and subcritical. The interrill soil erodibility factor (Ki) for the 12 years constructed soil was 1.03 x 10^6 kg s/m^4 which was lower than for the natural soil (1.82 x10^6 kg s/m^4) due to the higher resistance of the constructed soil. The estimated Ki values were in the range of the soils used for the WEPP model (*Water Erosion Prediction Project*). Thus, they can be used to predict soil loss by erosion on hillslopes at the studied locations and soil types by applying this model.

Key Words
Interrill erosion, detachment rate, minesoils.

Introduction
Soil water erosion is a process of detachment, transport and deposition of soil particles caused by kinetic energy of the raindrops impact on soil surface and the associate overland flow (Ellison 1946). The process of water erosion occurs in two forms: interrill and rill erosion (Meyer *et al.* 1975). In interrill erosion soil particle detachment occurs by the water raindrop impact on the soil surface and soil particle transportation by overland broad sheet flow is enhanced by the flow turbulence (Foster *et al.* 1985). Soil water erosion is a major environment issue in coal mine reclamation areas. Environment reclamation at Candiota coal mine produces constructed soils composed of a surface layer formed by the natural soil A horizon, frequently mixed with B and C horizons, and a subsurface layer formed by a heterogeneous mixture of rock and saprolite materials. The soil erodibility is the reciprocal of its resistance to erosion, representing its susceptibility to erosion at different rates, due to physical, chemical and mineralogical parameters (Wischmeier and Mannering 1969; Foster 1982). In the models that separate the erosion in rills and interrills, the interrill soil erodibility represents the proportionality constant between soil detachment rate and the rainfall intensity. The objectives of this study were to evaluate the flow hydraulic characteristics, to determine detachment rate and the interrill soil erodibility under simulated rainfall at laboratory conditions for a natural and a 12 years constructed soil from Candiota coal mine, RS, Brazil.

Material and methods
The tests were carried out in the Soil Erosion Laboratory of Soils Department at Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil. It used a 12 year old constructed soil and a natural soil (Paleudult) from the mine site, sampled in a coal mine located at Candiota, RS, Brazil. Soil samples were taken from the 20 cm topsoil, brought to the laboratory, air dried and passed through a 10 mm diameter opening sieve. An experiment was set up with an acrylic plot mounted on a 1.0 x 1.0 m metallic structure with useful area of 0.3481 m^2 (0.59 x 0.59 m), 0.10 m of depth and lateral edges 0.20 m of width. The plots were filled with a layer of 0.20 m crushed rock with 1.0 cm diameter, on which was placed a layer of 2.0 cm of sand and on top of these two layers it was placed a plastic screen with 1.0 mm opening. On this plastic screen was placed a 6.0 cm layer of air dried soil with bulk density of 1.3 g/cm^3. The soil in the plot was previously saturated for 24 hours. Simulated rainfall was applied at a water tension equivalent to 6

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centimetres of water column and the experimental plot adjusted to a slope of 0.09 m/m. The rainfall was applied using a rainfall simulator (Souza 1985; Mayer and Harmon 1979), with nozzles type *Veejet* 80.150 (from *Spraying Systems Company, Chicago,USA*); internal diameter of 12.7 mm; settled to 3.1 m from the soil surface with an exit pressure of water of 41 kPa, checked with a manometer. The rainfalls were applied during 90 minutes, with average intensity of 85 mm/h.

A. Hydraulics characteristics of the flow surface

The flow discharge rate (Q), in m^3/s, was determined by measuring the volume of runoff collected in plastic pots. The flow unit discharge (q) in m^2/s was calculated by dividing the total discharge rate by the plot width. The surface flow velocity (m/s) was determined by taken the time for a dye cover a fixed distance between two points in the plot at 5 minutes intervals. The average flow velocity was determined by multiplying the surface velocity by a correction factor (α= 2/3) (Farenhost and Bryan 1995; Katz *et al.* 1995). The flow depth (h) was determined according to Woolhiser and Liggett (1967) and Singh (1983), the Reynolds number (Re) according to Simons and Senturk (2002) and Froude (Fr) according to Chow (1959).

B. Determination of interrill erosion rates

The interrill soil detachment rate was determined by weighting the sediment collected during 1 minute in 1L plastic pots, at 3 minutes intervals throughout the time of the rainfall. After the weighting, it was added 5 mL potassium alum (50 g/L), for particles settling. After 24 hours, the excess of water was removed by suction and the pots with the sediment oven-dried at 50ºC until constant weight. The interrill soil detachment rate (Di), $kg/m^2/s$, was determined by the following relation:

$$D_i = \frac{Mss}{A\ D} \tag{1}$$

Mss = dry soil mass (kg); A = plot area (m^2); D = time of sampling (s).

The WEPP model (Flanagan and Nearinng 1995) consider that the interrill soil detachment rate at condition of bare soil, is given by:

$$D_i = K_i\ I^2\ S_f \tag{2}$$

D_i = interrill detachment rate ($kg/m^2/s$); K_i = interrill soil erodibility factor ($kg\ s/m^4$); I = rainfall intensity (m/s); S_f = soil slope factor. At the WEPP model (Liebenow *et al.*1990) the soil slope factor is adjusted by the equation:

$$S_f = 1{,}05 - 0{,}85e^{4sen\theta} \tag{3}$$

where θ represents the angle of slope (in degrees).

The interril soil detachment rate (Di) was determined at the experiment by an average of the last five measurements in each one of the four rainfall runs. Thus, with the known rainfall intensity and Sf factor adjusted for 0.09 m/m slope the interrill soil erodibility (Ki) factor may be determined by the following expression:

$$K_i = \frac{D_i}{I^2\ S_f} \tag{4}$$

K_i = interril fsoil erodibility factor ($kg\ s/m^4$); D_i = interrill detachment rate ($kg/m^2/s$); I = rainfall intensity (m/s); S_f = soil slope factor.

Results

The flow Reynolds number was 14.82 and Froude number 0.99 for the constructed soil and 14.03 and 0.62 for the natural soil (Table 1). Thus, these characterize a laminar and subcritical flow regime, as indicated by the values of Re < 500 e Fr < 1, respectively, typical of interrill erosion flow conditions. In Figure 1a and 1b it can be observed that the detachment rates presented a slight growing during the time of rainfall application, with tendency to become constant in last the 18 minutes, when they reached its maximum value. Thus, the average detachment rate in the last 18 minutes of rainfall was used for determination of interrill soil erodibility (Ki), with values of 2.62×10^{-4} $kg/m^2/s$ and 4.64×10^{-4} $kg/m^2/s$ for the constructed soil and natural soil, respectively, obtained as the average value of the last five determinations during the rainfall (Table 2). The average value of interrill soil erodibility (Ki) factor determined for the constructed soil was of 1.03×10^6 $kg\ s/m^4$, lower than the value for the natural soil, that was of 1.82×10^6 $kg\ s/m^4$ (Table 2). This may indicate that the constructed soil is more resistant to raindrop impact than the natural soil. One possible explanation is the type of structural units formed by the action of soil removal, disposal and reconstruction by heavy equipments that through compaction produced units that are very hard and resistant to the detachment by raindrop impact. The values of 1.03 x 10^6 and 1.82 x 10^6 kg s/m^4 determined for the interrill soil erodibility (Ki) factor for the constructed soil and natural soil, respectively, are within the range of values determined for soils that were used to develop the WEPP model (Alberts *et al.* 1995), between 0.5 and 12.10^6 kg s/m^4.

Table 1. Hydraulic characteristics of the interrill flow.

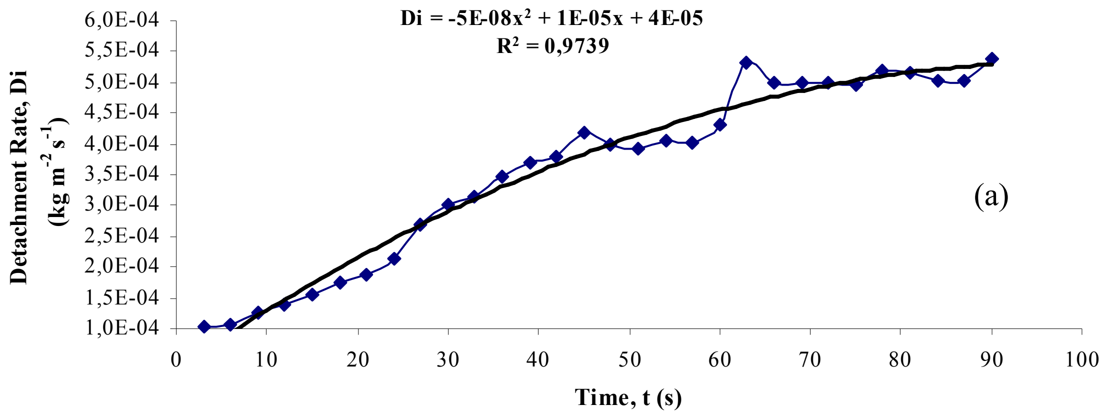
Soils	q	Vs	Vm	h	T	ν	Re	Fr
	m²/s	m/s	m/s	m	°C	m²/s	----adimensional-----	
CS 12 years	1,44E-05	0,076739	0,05116	0,000293	21,3	9,73E-07	14,82	0,99
Natural	1,32E-05	0,054928	0,036618	0,000372	22,75	9,43E-07	14,03	0,62

CS: constructed soil. q: net discharge by unit of width; Vs: surface velocity of the flow; Vm: average velocity of the flow; h: height sheet of the flow; T: temperature; **ν:** kinematics velocity; Re: Reynolds number; Fr: Froude number

Table 2. Detachment rate (Di) and interrill soil erodibility (Ki), Average of the four repetitions on rainfall with intensity of 85 mm/h(I =0,0000236 m/s) and slope of 0,09 m/m (Sf = 0,4560)

Soils	Di	Ki
	(kg/m^2/s)	(kg s/m^4)
CS 12 years	2,62 E– 04 b	1, 03 E + 06 b
Natural soil	4,64 E – 04 a	1,82 E + 06 a

CS: constructed soil. Followed values of same letters in the columns do not differentiate between itself for the test of Tukey to level of 5% of significance.



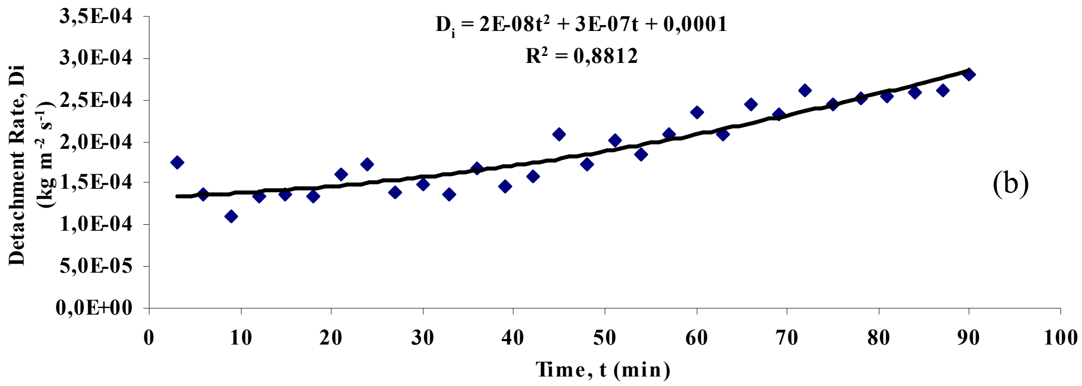


Figure 1. Interrill detachment rate of soil on simulated rainfall of 85 mm/h in slope of 0.09 m/m for: (a) natural soil; (b) constructed soil of 12 years old.

Conclusions

The flow hydraulic was laminar and subcritical for both soils studied, which are characteristic for interrill erosion conditions. The value of the interrill soil erodibility factor (Ki) determined for the constructed soil (1.03×10^6 kg s/m^4) was lower than the value obtained for the natural soil (1.82×10^6 kg s/m^4), values that are within the range for WEPP model (*Water Erosion Prediction Project*) prediction of soil loss erosion in hillslopes.

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Improvement of physical and chemical properties of Hungarian sandy soils by adding organic and inorganic amendments

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Abstract
The main purpose of the study was to investigate and compare the single and precomposted combined effects of different amount of organic (liquid manure, sewage sludge) and inorganic (bentonite, montmorillonite, $CaCO_3$) treatments on soil physical, chemical properties of sandy soils from Nyírség geographical area. Laboratory and field experiments were carried out for the study. The laboratory samples included sandy soil treated with increased amount of montmorillonite and bentonite; liquid manure; beet potash and the precomposted combinations of those. Sewage sludge compost was applied on the field. Rheological methods were applied to detect the changes in physical properties of soil samples.

Key Words
Organic and inorganic amendments, sandy soils, Rheology.

Introduction
One quarter of the total area of Hungary is covered by light textured soils, of which 16% is sandy, 9.5% is sandy loam. These soils occur in most of the genetic soil types (Várallyay 1984). Sandy soils are lacking organic and inorganic colloids. These are the reasons, why the fertility and the properties of these soils is determined by high water infiltration and weak water storage capacity, low available water and natural nutrient capacity, sensitivity for aridity and wind erosion (Várallyay 1984). Various and important experiments were carried out to improve sandy soils all over the world. The role of different soil constituents were explained by several authors (Volk and Hensel 1969; Troeh and Thompson 1993; Singh and Uehara 2000; Kay and Angers 2002).

Methods
Materials
Different compositions of organic and inorganic compounds were prepared for the laboratory investigations. The soil was classified as “Haplic Arenosol, Dystric” (WRB 2006). Different amounts of refuse bentonite, montmorillonite, beet potash and diary liquid manure were applied. In case of field samples 20 t/ha compost was applied. The compost contained: 40% fermented sewage sludge, 25% riolite, 15% bentonite, 10% lime and 10% straw. The soil was a “Lammelic Arenosol, Dystric” (WRB 2006).

Methods
Beside rheological measurements in soil suspension, the following soil chemical and physical investigations were carried out: Cation exchange capacity of the samples by modified Mehlich procedure (Buzás 1988), hygroscopic coefficient of the samples by Sík (hy1), simplified water retention capacity of the samples, simplified determination of 0.02 mm size particles in water and Na-pyrophosphate, micro-aggregate stability (dispersity factor according to Kacsinszkij and structural factor by Vageler) (www.soil-index.com).

Results
During the rheological measurements the initial maximum of the flow curves, τ_{inimax} (Pa) and the Bingham yield values were determined. The initial maximum is the maximum of the flow curves determined in the direction of the increasing velocity, and provides information on the structure of the soil, and the bonding forces at present. The Bingham yield value (B) is the value of the linear part of the curves projected to zero shearing stress, and provides information on potential aggregation in the decreasing velocity gradient range following the discontinuation of the shear stress.

Initial maximum of the flow curves
On increasing the bentonite content of the sand samples, the initial maximum of their flow curves increased. There was a strong linear correlation between the two parameters, with a Pearson's coefficient of 0.923. The relation was even stronger in case of samples containing beet potash and increasing amounts of bentonite. In this case Pearson's coefficient was 0.936.

At the same time, due to organic matter, Pearson's correlation coefficient was 0.847 when the samples contain two inorganic components besides the liquid manure (Figure 1). The explanation in this case could be that bentonite – organic matter – Ca agglomerates were formed that link sand particles together. The reason for the fact that the highest initial maximum values were not obtained from the samples containing both organic and inorganic additives could be that their organic component, due to its complicated structure, was very sensitive to external effects, such as shearing stress.

In case of field samples, the one from 2004, treated with compost could tolerate the highest shear stress. As an effect of the compost treatment, the strength of the bonds between the particles became stronger, due to the organic and inorganic additives within the compost. However, the treated samples from 2006 have produced similar results to those of the untreated samples, which suggest that as a result of the treatment the sample showed aggregation, but it was not present two years later at the second sampling. This was probably due to the repeated yearly disturbance, or the downward movement of organo-mineral complexes.

Bingham yield values
The rebuilding of the aggregates in the suspension was only observed in the case of samples with organic matter content, and not with samples containing only mineral materials (Figure 2). The reason for this was that the organic material, due to its great charges, could relatively quickly form organic matter – bentonite – Ca bridges after the disturbance, and that because of the presence of organic matter, microbial activity should also be considered. The fulvic acids formed during the microbial decomposition of unrecompensed dead organic residues and the Ca^{2+} ions in the system connected with the negative charges of the clay minerals.

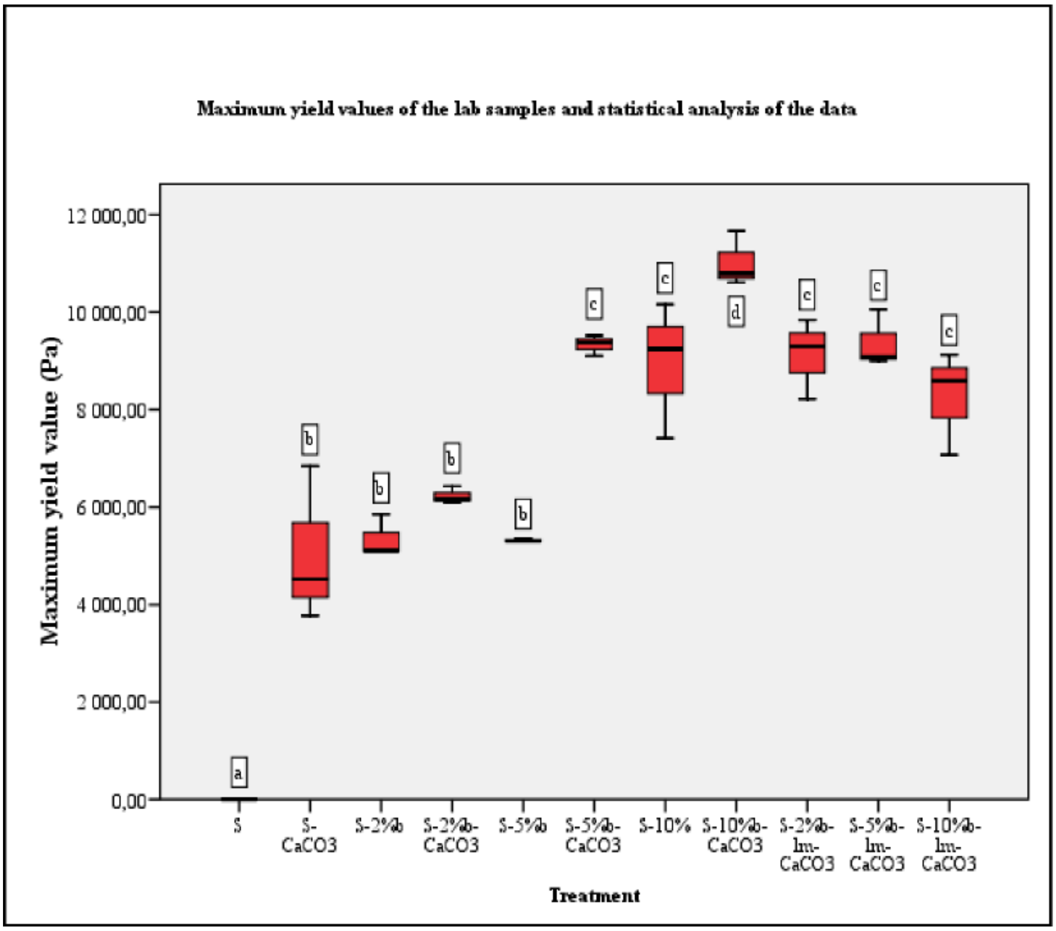

Figure 1. Maximum yield values of the flow curves of laboratory samples (significant differences are indicated with the lower case letters of the alphabet, with a confidence interval of 95%).

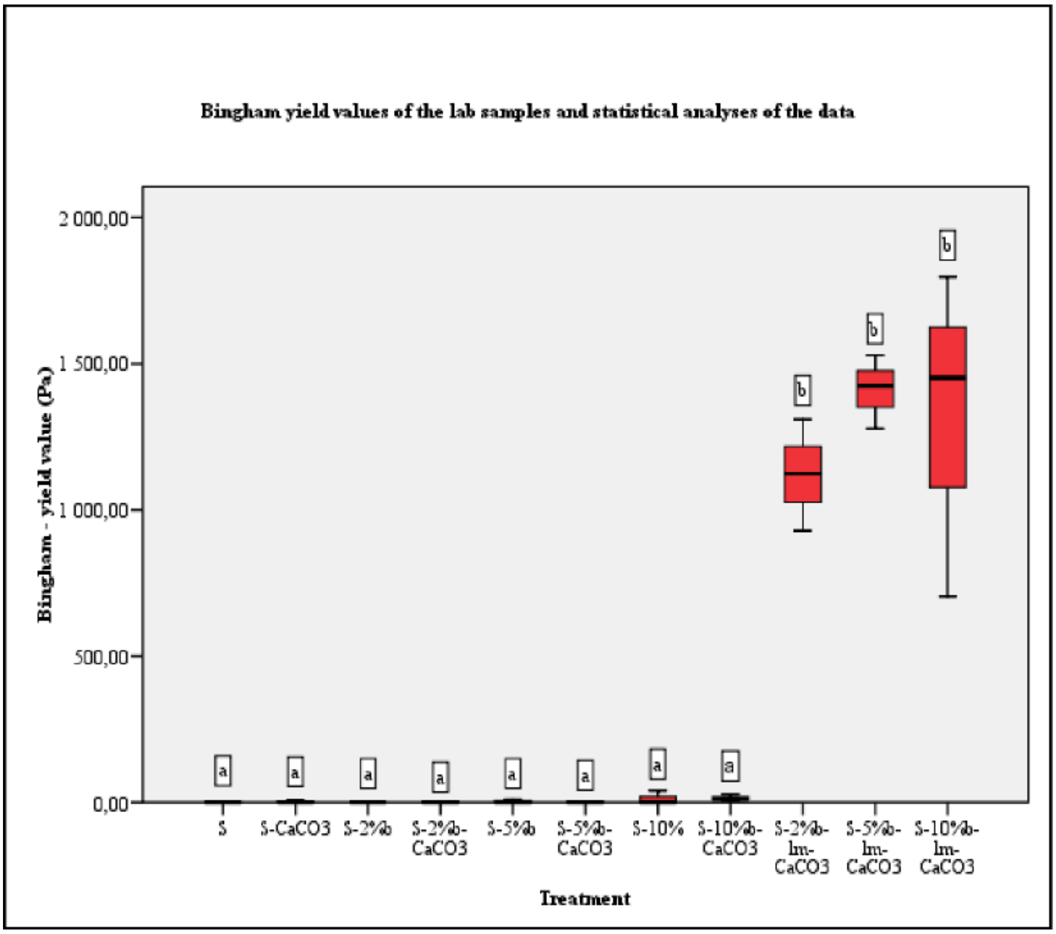

Figure 2. Bingham –yield values of the flow curves of laboratory samples, significant differences are indicated with the lower case letters of the ABC, with a confidence interval of 95%.

In the case of field samples, the one from 2004 treated with compost had the highest Bingham yield value, which means that as a result of the compost treatment, due to the organic and inorganic additives applied to the soil, the structure of the soil suspension showed re-aggregation after disturbance, on account of the increased number of bonding points. This effect could not be observed in the second sampling season, which could be because the organo-mineral complexes have either ceased to exist or moved to the lower layers.

The statistical comparison of the results of rheological measurements and results of traditional methods
Table 1 shows the correlation comparison of the results from Rheology and the applied measurements indicated by the Pearson's correlation coefficient.

Based on the results it can be concluded that a linear relationship could be observed between the initial maximum of the flow curves (τ inimax), the results of hy1 and cation-exchange capacity. That was, on the application of organic and inorganic additives, if we increase the colloid content (and charge) of the soil, it also increased the maximum shear stress it could tolerate. The Bingham – yield values showed strong correlation with the results of the water retention measurements. This means that if the soil's water-holding capacity increases, so does its ability to re-aggregate in? suspension after the end of the stress it was exposed to. The Bingham – yield values showed a strong medium connection with dispersed particles content in water, and a weak medium connection can be observed with the dispersed particles content in Na - pyrophosphate.

Table 1. The statistical comparison of the results of rheological measurements and results of traditional methods; *: correlation is significant at 0.05 level, **: correlation is significant at 0.01 level; n.c.: no correlation.

	Water retention	Dispersed particles in water	Dispersed particles in Na-pyrophosphate	Vageler structure factor	Kacsinszkij dispersion factor	hy1	CEC
τ inimax	0.444*	0.391*	n.c.	n.c.	n.c.	0.788**	0.820**
Bingham yield value	0.985**	0.666**	0.497**	n.c.	n.c.	n. c.	n. c.

Conclusion

Clay minerals, rocks containing clay minerals and also materials containing $CaCO_3$ have a significant effect on soil properties. Due to their colloid and adhesive properties, they increase the strength of bonds between soil particles. Both physical and chemical measurements properties showed better improvement when the organic and inorganic components were precomposted before application. The addition of beet potash resulted in further favorable effects on the results of water retention capacity and rheological measurements. Rheology proved to be a suitable method to track changes in soils resulting from the addition of different mineral and organo-mineral materials. It provides quantitative measures of the forces linking together the soil particles (maximum yield value, Bingham – yield value). The results of rheological measurements can be compared and do show a certain level of similarity with other methods for measuring different soil chemical and physical parameters. In soils it is primarily the „newly added" organic material content that takes part in the re-aggregation of the suspension structure after disturbance, as opposed to the mineral components.

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Modeling runoff and erosion from construction sites in 2-D with RUSLE2

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Abstract
New techniques allow RUSLE2 to estimate average monthly runoff, the number of runoff events per year, and parameters describing the statistical distribution of runoff event depths for any combination of location, soil, and management. This allows the determination of runoff events of specific return periods and erosion computation during an accounting period for a representative sequence of runoff events that is based completely on existing RUSLE2 input information. Further, the RUSLE2 code has been modified to allow efficient grid-based sheet and rill erosion computations that can be driven by high-resolution elevation data. Local slope length is determined using the ratio of runoff entering a cell to that leaving the cell, thus reflecting upslope variation in soil and land use. Surface roughness, residue cover, and soil biomass properties are re-used for each combination of soil and management, creating computational efficiency. These developments overcome the limitations of having to describe a construction site as a series of one-dimensional representative profiles, allowing RUSLE2 erosion and sediment delivery computations to be applied in a GIS context to conduct "before" and "after" analyses of construction sites while making use of recent advances to the database and results reporting capabilities described by Yoder *et al.* (2007).

Introduction
RUSLE2 is the most recent in the family of USLE/RUSLE/RUSLE2 models proven to provide robust estimates of average annual sheet and rill erosion from a wide range of land use, soil, and climatic conditions. RUSLE2's capabilities have been expanded over earlier versions using methods of estimating time-varying runoff and the CREAMS process-based sediment transport routines so that it can estimate sediment transport/deposition/delivery on complex hillslopes. In addition, while RUSLE2 is generally driven with readily-available monthly climate information, calculations are done on a daily time-step, allowing the use measured or generated daily rainfall and erosivity values where those data are available.

RUSLE2 is a land use-independent model that has been widely used for conservation planning on construction sites by engineers, planners, reviewers, inspectors, and developers. Yoder *et al.* (2007) described enhancements made to the RUSLE2 interface and databases to facilitate this application. These enhancements include database descriptions of management practices such as mulches, blankets and vegetations, devices or structures such as permeable barriers (e.g., silt fences, straw bales, fiber rolls, compost socks, etc.) and sediment basins, and combination techniques such as vegetative filter strips. A major advance in results reporting was the definition of an "accounting period," the period of interest during which the construction planner is responsible for controlling sediment delivery from a site. Though the definition is flexible, in the example cited in Yoder *et al.* (2007), the accounting period begins with the first soil disturbing field operation and ends with the application of permanent erosion protection, defined as either application of a semi‐permanent non‐erodible surface (pavement, landscape fabric and cover, sod, etc.) or a specified period of growth of a perennial vegetation. The default for this period is 60 days of growth during which the average air temperature was above 1.7°C, thereby giving no growth credit for periods when vegetation is dormant. This approach gives the planner an incentive to keep the accounting period short, to reduce erosion and delivery during that period, to plan construction during non‐erosive periods, and to plant cover when it will grow, all of which are good conservation planning practices.

Two limitations with the current RUSLE2 for conservation planning of construction sites are that (1) the planner must define a representative one-dimensional hillslope profile, or series of profiles, to characterize the site both before and during construction, and (2) that erosion caused by concentrated flow in channels is not estimated. The purpose of this manuscript is to describe a new 2-D version of RUSLE2 that overcomes the first limitation and new RUSLE2 runoff-estimation techniques that allow direct linkage to a channel erosion model to overcome the second.

Grid-Based RUSLE2

GIS-based tools are being developed by Agren, Inc. (http://www.agren-inc.com/projects.php?proj=15) to allow high resolution LiDAR elevation data to be used with RUSLE2 to improve conservation planning on agricultural lands in Iowa. Since each RUSLE2 hillslope profile terminates at a location where overland flow intersects a concentrated flow channel, identification of the location of channels (including terrace channels and ephemeral gullies) within agricultural fields is a critical step in the process. Because detailed CAD drawings are usually available that describe the topography of construction sites very precisely, and the location of channels is often controlled by design, the new technology can be readily adapted to conservation planning on construction sites.

To improve computational efficiency and enable the automatic determination slope lengths in complex topographic settings, RUSLE2 was re-coded to allow re-use of common information in grid-based calculations (Figure 1A). The calculation of soil biomass, soil residue cover, soil roughness, and similar properties for every day of a simulation is one of the most time-consuming steps in RUSLE2 computations, so reusing this information for the limited number of soil and management combinations found in a typical site simulation greatly reduces the runtime of a grid-based simulation. Further, the determination of slope lengths as the ratio of runoff entering a cell to that leaving the cell has been integrated into the RUSLE2 engine (Figure 1C). This allows the automatic determination of an equivalent slope length, matching the results of the standard equations for uniform profiles yet permitting the correct representation of complex situations involving topographic flow convergence as well as seasonal and spatial variability in runoff generation related to soil and management combo effects.

A shell program was developed that sets up and executes RUSLE2 hillslope simulations using functions provided by the Application Programming Interface (API), distributed in the RUSLE2 .dll. The shell program defines input parameters and some RUSLE2 simulation options, executes the erosion simulation and retrieves computed erosion values, optionally links results to a channel erosion model, and displays results on the screen. The method is structured in three independent phases. Phase 1 encompasses most of the user interaction through a graphical interface and consists of identifying the simulation area, generating soil and management layers, retrieving a DEM in the required resolution, and then determining drainage networks and the locations of the concentrated flow channels that end RUSLE2 hillslope profiles. In Phase 2, the shell program sets up the RUSLE2 model for the 2D simulation area, executes the simulations, and exports simulation results for post-processing. Phase 3 converts simulation results into user-friendly formats such as maps, graphs, and summary tables according to user requirements. The computational module of Phase 2 accesses RUSLE2's computational engine through its DLL. It utilizes data layers prepared in Phase 1 (flow directions, slope steepness, soil map, management map, and channel network cells), and user-defined parameters such as RUSLE2 simulation options and requirements for data output. The module efficiently divides the simulation area into a number of profiles with varying numbers of raster cells, and manages the execution of the simulations through RUSLE2 API functions. RUSLE2 outputs of distributed soil erosion, sediment delivery to channels, and sediment deposition in channels and sediment basins are retrieved and saved. Optionally, channel erosion can be estimated by linkage of RUSLE2 results with a channel model as described in the next section.

Each cell crossed by a channel defines a drainage area outlet, corresponding to the end of an overland flow path. For each channel-containing cell in the network, the flow directions map is analyzed to determine which of the neighboring cells drain to that channel cell. The process is recursive and somewhat complex: if a cell drains into the cell being inspected, focus is shifted to that second cell. This process is repeated in checking uphill cells uphill until no inflow is detected for a cell. The no-inflow cell identifies the beginning of a flow path. The cell is marked and numbered. A reverse process is then started, following flowpaths downhill, defining the connectivity among the several cells that compose the area draining to the original channel cell. The process is repeated for each channel cell in the network. A RUSLE2 profile is thus created for each channel cell (Figure 1B). The channel cell itself is divided by the channel and potentially contributes to the slope length of the left and right bank overland flow paths. Each 2-D RUSLE2 profile therefore comprises an ordered collection of raster cells. RUSLE2 internally manages the transfer of runoff and sediment among the profile segments, but the sequence of computation follows the cell interconnectivity prescribed to RUSLE2 by the shell program for each profile. The RUSLE2 profiles can be computed independently, in any order, which permits optimization through parallel computations in multiprocessor or multicore computers.

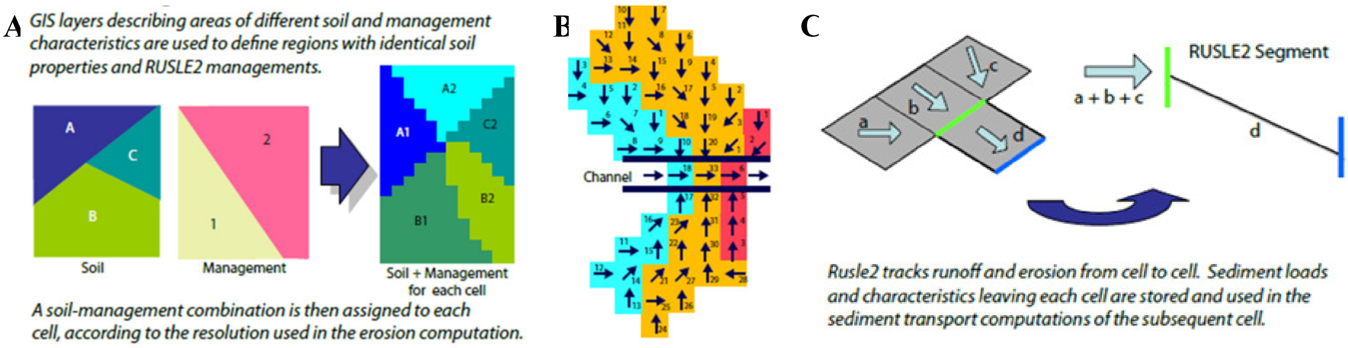

Figure 1. (A) Unique combinations of soil and management are termed "combos" and the resulting residue, roughness, and soil biomass properties for each day of the simulation are stored internally in RUSLE2 for efficient reuse. (B) Starting with each channel cell (black outline), a computer algorithm analyzes the flow directions map to determine the connectivity and computational sequence of the cells that compose a profile. The figure shows three profiles on each side of the channel, identified in different colors. (C) RUSLE2 determines effective slope length based on the ratio of runoff leaving a cell to that entering the cell, enabling the appropriate accounting for topographic, soil, and management effects on local erosion estimates.

Runoff Event Estimation

Dabney *et al.* (2010) proposed and evaluated a method for predicting a series of representative runoff events whose sizes, durations, and timing are estimated from information already in the RUSLE2 database. They developed regression relationships to approximate the mean monthly runoff, annual runoff event frequency, and a gamma distribution function scale parameter that characterized 30-year stochastic runoff predictions generated using the AnnAGNPS model (Bingner and Theurer 2001). These algorithms have now been coded into RUSLE2 so that the size of the runoff event with any return period can be estimated, allowing RUSLE2 to be used in risk assessment calculations. By assuming that the largest in a series of runoff events that cause annual average channel erosion had a 1-year return period ($Q_{1y,24h}$) and that the depths of the periodic runoff events were proportional to long term average daily runoff amounts, the dates and sizes of a representative runoff event sequence are now calculated within RUSLE2. The largest runoff event in the sequence defaults to $Q_{1y,24h}$, although a different maximum event can be selected; the sum of all runoff events approximates the annual runoff for any location, soil, and management combination; and the sum of sheet and rill erosion estimates from all events is very similar to the RUSLE2 estimates computed using normal procedures.

For application to construction sites, the portion of the annual series of events occurring during an accounting period can be used to efficiently drive grid-based computations of sheet and rill erosion and sediment delivery to channels. Further, the available event outputs of runoff depth, runoff rate, runoff concentration, and fractional contributions of sand, silt, clay, small aggregates, and large aggregates make it possible to link RUSLE2 outputs to a channel erosion model. Dabney *et al.* (2010) illustrated the procedure by linking RUSLE2 output to the channel erosion routines used in CREAMS (Foster *et al.* 1980), which are essentially the same as those used in the watershed version of WEPP (Ascough *et al.* 1997) and GeoWEPP (Renschler 2003) to estimate ephemeral gully erosion. The same approach could be applied to estimate erosion of potential channels in alternative construction site designs.

Summary

RUSLE2 offers a simple yet robust system for estimating sheet and rill erosion from hillslopes. Extensive databases exist for soils, climates, operations, vegetations, and residue descriptions that can be readily extended to other locations. New techniques have been developed to allow average monthly runoff estimation that can be adapted to most temperate regions of the world and could be extended to tropical regions with additional development. The RUSLE2 computational engine has been re-coded to allow efficient computation of sheet and rill erosion on a grid basis. Where high resolution elevation data are available, as is usually the case on construction sites, a variety of GIS tools can be used to create raster maps of flow direction, slope steepness, soil, management, and location of concentrated runoff channels. A shell program uses these raster maps to determine RUSLE2 profiles that end at each channel cell and calls the RUSLE2 calculation engine to determine distributed estimates of sheet and rill erosion. The results of these computations can optionally be linked to a concentrated flow erosion model if channel erosion is a resource concern at the site. Erosion and site sediment losses can be determined and reported for an accounting period that begins with the first site disturbance and extends until permanent cover is established. By allowing representation of complex two-dimensional topography and spatial variation in soil and land management properties, these developments allow RUSLE2 to be a state of the art tool conservation planning and stormwater management on construction sites.

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Purification performance of the FWS constructed wetland in biotope area over three years

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Abstract
The effluent from the combined household wastewater treatment facilities used in unsewered areas of Japan is generally high in N and P. In Japan, environmental quality standards for Zn pollution were enacted recently because of the toxicity of Zn to aquatic ecosystems. In 2004 a fallow paddy field at the Koibuchi College of Agriculture and Nutrition was converted into a surface-water-flow constructed wetland (500m^2) to clean the effluent from the combined household wastewater treatment facility of a dormitory (100 residents) before discharge to a pond. We evaluated N and P removal efficiencies and the fate of Zn in the wetland from February 2006 to March 2009. Wetland influent contained an average of 20.9 mg/L total N and 2.01 mg/L total P. In the effluent from the wetland, average total N concentration was 11.3 mg/L and average total P was 0.98 mg/L. Average Zn concentration decreased from 0.046 in the influent to 0.027mg/L after passing through the wetland. The constructed wetland system was effective for removing not only nutrient salts but also Zn from secondary treated domestic wastewater. N, P and Zn removal mechanisms are discussed in terms of the material balance and the first order reaction model.

Key Words
Constructed wetland, nitrogen, phosphorus, zinc, *Zizania latifolia,* first-order rate cosfficient.

Introduction
In areas of Japan where no sewerage systems have been constructed, domestic wastewater is usually treated by combined household wastewater treatment facilities (these facilities include primary and secondary treatment processes). Effluent from these kinds of systems generally contains relatively high levels of nitrogen (N) and phosphorus (P). Environmental quality standards for zinc (Zn) pollution were enacted recently in Japan because of the toxicity of Zn to aquatic ecosystems. The water quality standard for Zn in rivers and lakes is 0.03 mg/L, and the wastewater quality standard is 2 mg/L. Wastewater from a dormitory at the Koibuchi College of Agriculture and Nutrition in Ibaraki Prefecture, central Japan is treated by a combined household wastewater treatment facility. N and P in the wastewater are not removed sufficiently, although organic matter is well decomposed. The effluent was being discharged into an irrigation ditch that flowed into a pond for agricultural use. Algal blooms sometimes appeared in the pond, and the major nutrient source was considered to be effluent from the dormitory. In recent years, considerable attention has been directed toward constructed wetlands, because of their low cost and ease of operation (Brix 1993; Vymazal 2007; Cooper 2007). In 2004, about 0.2 ha of fallow paddy field at the college was converted into a biotope containing a 0.05-ha surface-water-flow constructed wetland to clean the effluent from the dormitory before discharge to the pond, as well as to educate students on environmental issues. Because the zone is surrounded by rice fields and because it was to be managed as a biotope, we chose the indigenous *Zizania latifolia* (wild rice) for the constructed wetland vegetation because of concern that other plants (especially *Phragmites australis* (common reed)) might invade the rice fields and puncture their bunds. We were also concerned that any exotic species used could become weeds.
We had already reported on the N, P and Zn removal efficiencies in the constructed wetland system around a year (Abe *et al.* 2008). In this paper we evaluated removal efficiencies of those pollutants in this wetland over three years by using first order reaction model. We also discussed the influence of temperature on the removal efficiencies.

Methods
FWS constructed wetland in Koibuchi Collage
The constructed wetland is a free-water-surface flow (FWS) type about 500 m^2 in area and 0.1 m deep, planted with *Z. latifolia* at the time of its creation. The wetland soil was Humic Gleyed Andosol. To prevent water from flowing directly to the exit, baffles were installed in the wetland to make the water flow through

a circuit (Figure 1). The wetland receives secondary treated wastewater (about 26 400 L/d, or 52.8 $L/m^2/d$ of wetland) from a student dormitory with about 100 residents; there is therefore about 5 m^2 of constructed wetland per dormitory resident. Water purified in the constructed wetland flows through the biotope area, mixes with rice field drainage, spring water, and other water, and then flows out of the biotope zone and into the holding pond.

Measurements

The volume of wastewater inflow was measured with an integration flow meter. The effluent water volume was calculated as the sum of inflow and rainfall minus evapotranspiration. Because the ground water level is high in the biotope area, water leaching is considered to be negligible. For convenience, the typical rate of evapotranspiration from a Japanese paddy field was substituted for that from this constructed wetland. The water quality was analysed weekly from April 2006 through March 2009. Inorganic N and PO_4-P were measured by ion chromatography (IC7000, Yokogawa). Total N (TN) and total P (TP) concentrations were measured with an autoanalyser (TRAACS 2000, Bran +Luebbe) after potassium persulphate and sodium hydroxide digestion. To measure acid-soluble Zn concentration, water samples were adjusted to pH 1 with nitric acid just after sampling. To measure dissolved Zn concentration, water samples were filtrated with 0.2μm membrane filter. Zinc concentration was measured with an inductively coupled plasma optical emission spectrometer (Vista-Pro, Varian). The aboveground parts of Z. latifolia growing over an area of 1m^2 were harvested at 5 points in the constructed wetland. Samples were dried at 80C for 3 days and then milled to fine powder. The N concentration was measured with NC analyzer (SUMIGRAPH, Sumika Chemical Analysis Service). After acid digestion of the powder, the P concentrations were measured by autoanalyzer and the Zn concentration by inductively coupled plasma optical emission spectrometer

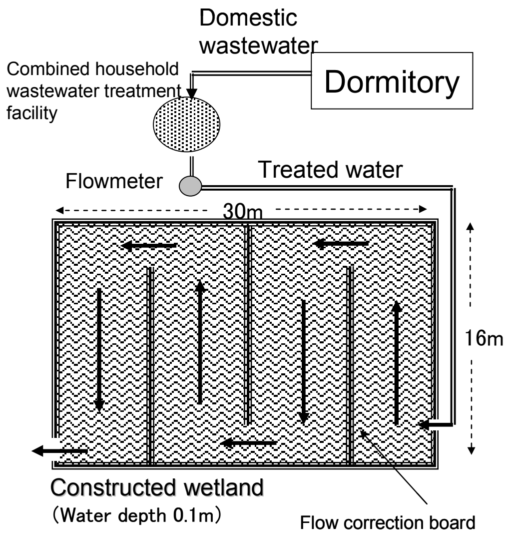

Figure 1. FWS constructed wetland in biotope area in Koibuch College.

Results and discussion

Figure 2 illustrates the concentrations of TN, TP and acid-soluble Zn concentration (in 0.1 mol/L HNO_3 solution) in the influent to, and effluent from, the constructed wetland. Table 1 shows average concentrations of N, P and Zn compounds in the influent to, and effluent from, the constructed wetland.

TN, TP and acid-soluble Zn in the influent were removed effectively by the constructed wetland system. On average, the influent to the wetland (i.e., the effluent from the wastewater treatment facility) contained 20.9 mg/L TN and 2.01 mg/L TP. In the effluent from the wetland, average TN concentration was 10.3 mg/L (46% reduction) and the average TP concentration was 0.98 mg/L (51% reduction). The average acid-soluble Zn in the influent was 0.046 mg/L. Acid-soluble zinc was almost the same as total zinc: the slope of the linear regression between total and acid-soluble Zn concentrations was 0.959, quite close to 1 (Abe *et al.* 2008). Therefore, the fate of acid-soluble Zn was considered to reflect total Zn behaviour. The average acid-soluble Zn concentration in the effluent was 0.027 mg/L (41% decrease). Our findings indicate that the constructed wetland system effectively decreased the Zn concentration in the secondary treated domestic wastewater to below the water quality standard level. Most studies of heavy-metal treatment in constructed wetland systems have examined heavily contaminated wastewater from mine drainage and industry (Mays and Edwards 2001). In contrast, our results indicated that a constructed wetland planted with *Z. latifolia* was useful for treating wastewater with a low Zn concentration; the system decreased the Zn concentration to a level that was unlikely to have negative effects on the aquatic organisms downstream.

The influent to the wetland contained 10.8 mg/L NO3-N, 8.5 mg/L NH_4-N and 1.5 mg/L organic + particulate N. These values indicated that organic compounds were decomposed successfully in the combined household wastewater treatment facility (Table 1). Inorganic N, PO_4-P and dissolved Zn was removed mainly by the constructed wetland system. The organic + particulate N, P and particulate Zn concentration hardly decreased while the effluent was passing through the wetland; therefore, the major mechanism of N, P and Zn removal in the wetland appears to be plant uptake and/or physicochemical reactions, rather than precipitation of particulate N, P and Zn.

Table 1. Average concentrations of N, P and Zn compounds in the influent to, and effluent from, the constructed wetland.

Conpounds	Influent (mgL^{-1})	Effluent (mgL^{-1})	Remarks
TN	20.9	10.3	Average during 3 years (n=157)
NO3-N	10.8	5.4	
NH4-N	8.5	4.3	
Org + particulate N	1.5	1.3	
TP	2.01	0.99	Average during 3 years (n=157)
PO4-P	1.42	0.44	
Org + particulate P	0.61	0.54	
TZn	0.37	0.11	Average of selected samples (n=10)
Dissolved Zn	0.27	0.03	
Particulate Zn	0.04	0.07	

Figure 3 illustrates the material balance of the constructed wetland during the period from April 2007 to March 2008. Yearly loading to the wetland was 335 g/m^2 for TN (0.92 $g/m^2/d$) and 33 g/m^2 for TP (0.09 $g/m^2/d$). The removal amount was 131 g/m^2 for TN (0.36 $g/m^2/d$) and 17.0 g/m^2 for TP (0.05 $g/m^2/d$)., giving percentage removal rates of 39.2% and 50.8%, respectively. Thirty eight g N and 5.4 g P had accumulated in the aboveground parts of *Z. latifolia* per 1 m^2 of the wetland. As a proportion of the yearly removal by the constructed wetland system this amounted to 29.0% of the N and 32.2% of the P removed. Yearly Zn loading was 0.560 g/m^2 (0.0 15 $g/m^2/d$). The yearly Zn removal amount was 0.367 g/m^2 (0.001 $g/m^2/d$), and the percentage removal rate was 65.5%. The amount of Zn accumulated in the aboveground parts of Z. latifolia corresponded to 8.5% of the Zn removed by the constructed wetland system over a year.

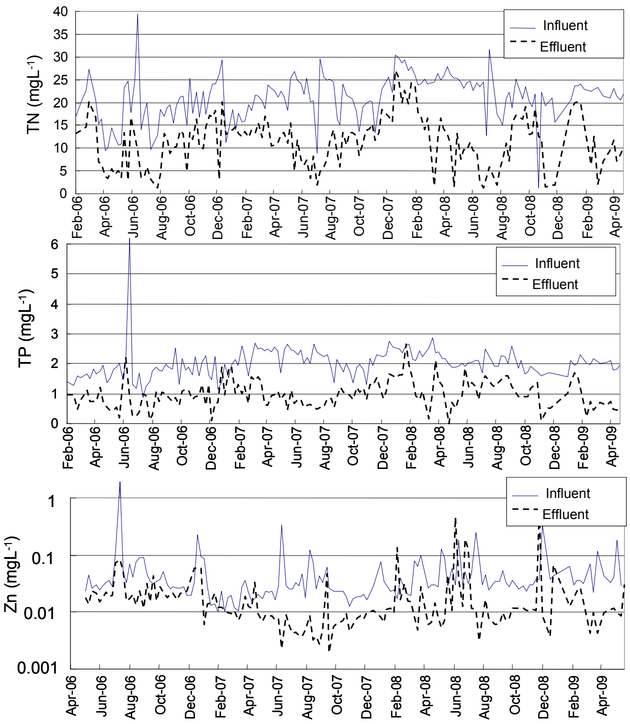

Figure 2. TN, TP and acid-soluble Zn concentrations in the influent to, and effluent from, the constructed.wetland.

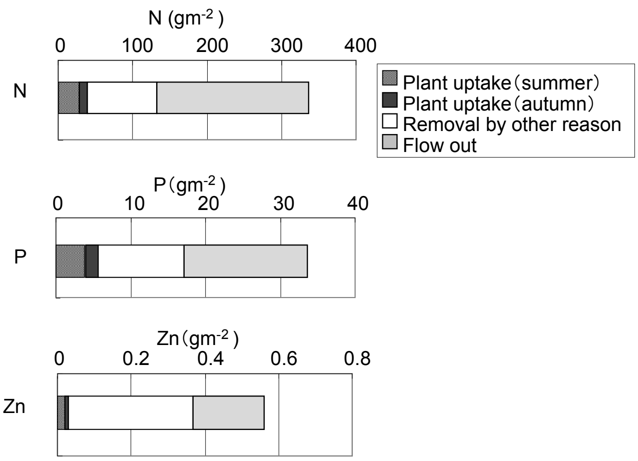

Figure 3. N, P and Zn balance during the period from April 2007 to March 2008.

N, PO4-P and acid soluble Zn concentration in the wetland decreased with distance from inlet (data not shown). Then assuming that inorganic N, PO4-P and acid soluble Zn concentration were reduced by first order reaction and water flow in the wetland was plug-flow, first order areal rate coefficient (k) was calculated by the following equation. Ln(C/Co) =-k/q, where C is the effluent concentration, Co is the influent concentration, k is the first order areal rate coefficient, and q is the hydraulic loading rate (q=Q/A). The rate coefficient for inorganic N reduction was well correlated with temperature. It indicated that N was removed mainly by biological reaction like denitrification. On the contrary, k for PO4-P and acid soluble Zn reduction did not change synchronously with temperature. It indicated that P and Zn were removed mainly by physicochemical reaction. Taken together, our results suggest that N was removed mainly by denitrification and partly by plant absorption, and that P was removed mainly by adsorption to soil particles and partly by plant absorption. Our results also suggested that Zn was removed mainly by physicochemical reactions, such as by adsorption to soil particles and organic matter in the constructed wetland.

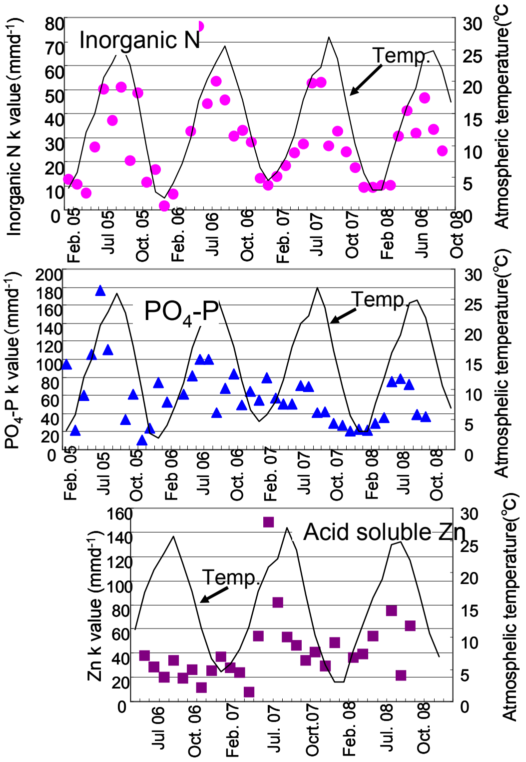

Figure 4. Changes in first order rate coefficient (k) for inorganic N, PO_4-P and Zn reduction.

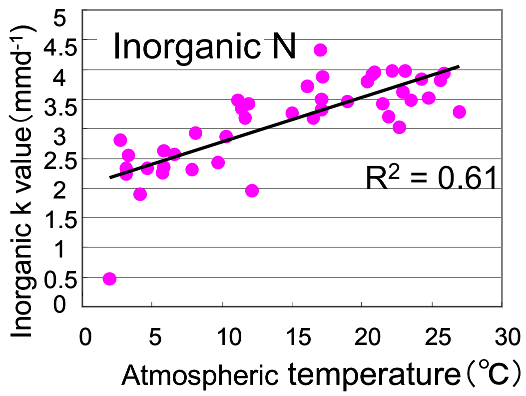

Figure 5. Relationship between first order rare coefficient (k) for inorganic N reduction and atmospheric temperature.

Conclusion

The FWS constructed wetland planted with *Zizania latifolia* was effective for removing not only nutrient salts but also dissolved Zn from secondary treated domestic wastewater over three years. The material balance in the wetland and the analysis on the first order rate coefficient for N, P and Zn reduction suggested that N was removed mainly by denitrification and partly by plant uptake, P was removed mainly by adsorption to soil particles and partly by plant uptake and Zn was removed mainly by adsorption to soil particles and organic materials.

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Studying the Philip model capability to estimate water infiltration parameters

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Abstract
Infiltration refers to the entry of water into a soil profile from the boundary. Generally, it refers to vertical infiltration, where water moves downward from the soil surface. The Philip model is one of the infiltration models with an algebraic equation based on sound physical reasoning for vertical infiltration under ponded conditions. We designed a program in Quick Basic software and wrote algorithms for three models that include Kostiakove, Modified Kostiakove and Philip. Afterwards we gathered factual infiltration data by the double ring method in 12 soil series of Saveh plain in Markazi province in Iran. After assessing model coefficients, these equations were regenerated by EXCEL software and calculations related to observations and related graphs were done. Infiltration parameters, such as cumulative infiltration and infiltration rate were obtained from the models. Then observed and determined parameters of infiltration were compared. Results showed that for seven series the Philip model could determine the infiltration parameters with a good agreement. Also the Philip model for five series of soils, after passing of time, had a curve shape as shown in the Philip model for Saveh (2), Labar (1), Harisan (2), Gharehtappeh and Anjilavand series, including 5 series with heavy to very heavy texture. The sorptivity coefficient of the Philip model became less than zero, for long times, consequently accumulative infiltration decreased during this period. Other models particularly Modified Kostiakove could quantify amounts of cumulative infiltration and infiltration rate. In the short and middle time for most series, Kostiakove and Modified Kostiakove models were better than the Philip model in estimating infiltration parameters. However for long times the Philip model could determine infiltration parameter better than the other models.

Key Words
Infiltration, model, Kostiakove, modified Kostiakove, Philip.

Introduction
Infiltration phenomenon explain water entering into the soil in a vertical direction, therefore this process needs to suitable model for simulation. Equations, have been designed according to the type of model (experimental or analytical models) and have various and different capabilities. A combination of Darcy's law and flow continuity equation provides a general water flow equation for unsaturated soils. The simplest application for this equation is for describing horizontal water into soil infiltration. If relationships between water and soil matric potential and hydraulic conductivity are defined, then a description of the infiltration phenomenon by solving Richard's equation is possible. Using a serial hypotheses in solving Richard's equation, is inevitable. In solving the Richard's equation, soil physical parameters are often consider fixed, but these parameters may change and determining these changes and entering them in the Richard's equation is difficult. Philip (1, 2) was the first to solve Richard's equation for unsaturated flows as a serial of potential functions. His hypothesis considered a unit soil with infinite depth and some primary fixed water as a thin layer of water. The structure of this research is based on analysis of the Philip model's capability in determining accumulative infiltration quantities compared to real quantities.

Methods
The study area was located on the Saveh Plain (491109ha) covering 12 soil series.

By the method of double ring in filtration and three repetitions in any series, cumulative infiltration quantities were obtained. In the studied series, accumulative infiltration quantities after determined times and terminal infiltration velocity, calculated traits were determined. In this research three models of water infiltration into the soil, consisting of the Kostiakove, Modified Kostiakove and Philip models were assessed. After designing models algorithms in QUIC BASIC software, the coefficients of models were obtained from experimental data. In the Kostiakove model we took logarithms from both sides of the the equation to make a linear equation:

Table1. Characteristics of soil series according the Soil Taxonomy.

Soil Taxonomy		Percentage of Area	Area(ha)	Soil series	Land Physiography	Row
Family	Order					
Fine,Mixed,Thermic	Aridisols	2.10	5017	Dolatabad	Piedmont Alluvial Plain	1
Fine,Mixed,Thermic	Aridisols	8.17	8730	Harisan		2
Fine,Mixed,Thermic	Aridisols	2.5	2560	Masoomabad	River Plain	3
Fine,Loamy,Mixed,Calcarous,Thermic	Entisols	1.8	3960	Saveh		4
Fine,Mixed,Thermic	Aridisols	4.15	7555	Anjilavand		5
Fine,Mixed,Thermic	Aridisols	5.6	3200	Gharehtappeh		6
Very Fine, Carbonatic,Thermic	Aridisols	5.4	2210	Akbarabad	Low Land	7
Very Fine, Carbonatic,Thermic	Aridisols	1.1	540	Abbasabad		8
Very Fine, Carbonatic,Thermic	Aridisols	7.25	12630	Labar		9
Fine,Loamy,Mixed,Calcarous,Thermic	Entisols	5.2	1218	Gharehchay	River Trace	10

Log (I) =log (a) + (b) log (t)

In this equation (b) is slope, and log (a) is intercept. Values of (b) and log (a) can be derived from graphs of log time versus log cumulative infiltration.

In the Modified Kostiakove model, by dividing of both sides of the equation by t, the following equation is obtained:

$$\frac{I}{t} = a\ t^{(b-1)} + c$$

Values of (a) and (c) coefficients are calculated by regression.

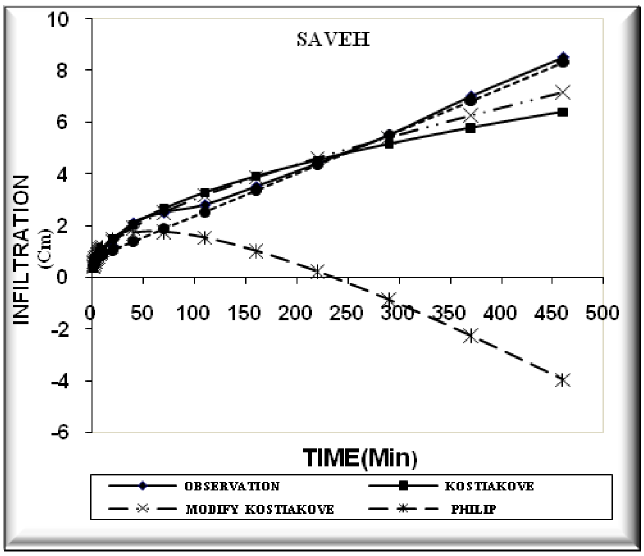
In the Philip model, by dividing of both side of equation on (t) we will have:

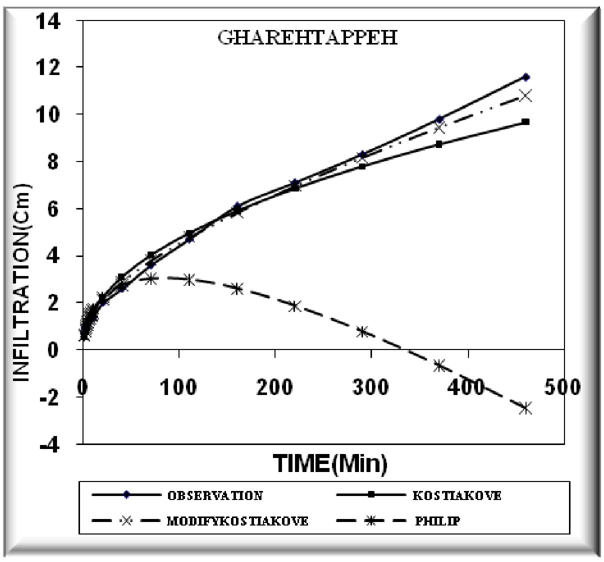
$$I / t = S \frac{1}{t^{1/2}} + A$$

Coefficients A (Soil hydraulic conductivity function) and S (Sorptivity coefficient) were determined by regression. After assessing to models coefficients, these equations were regenerated by EXCEL software and calculations using the models were related to observations.

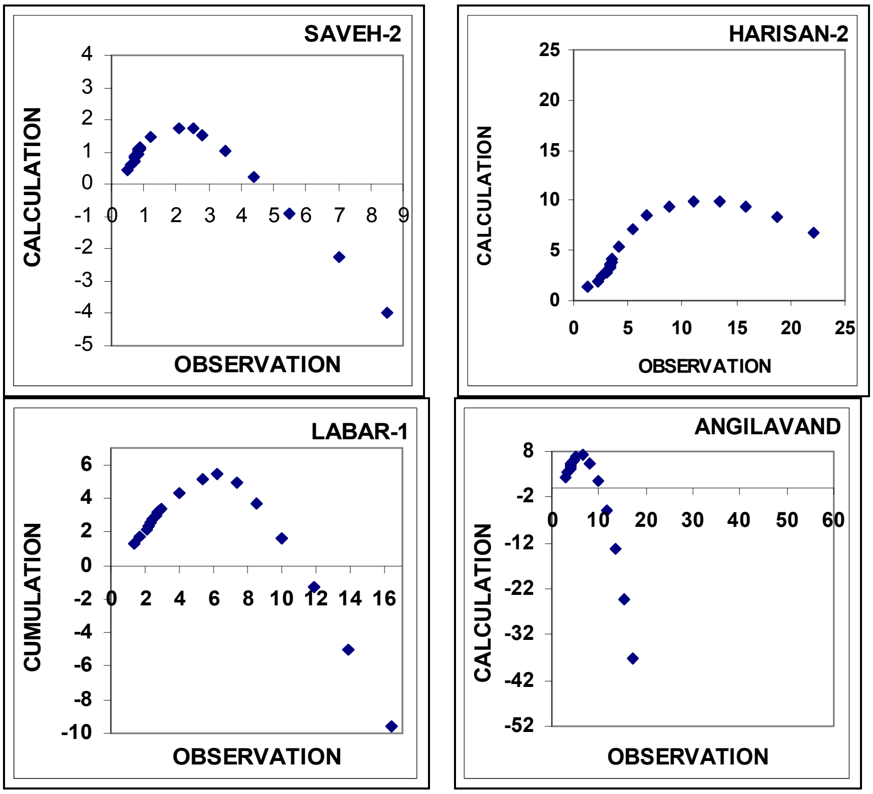
Results

After calculation of coefficients, we used of these models for calculation of cumulative infiltration and infiltration rate, that we compared with observations.





Graphs1 and 2. Comparative plots of cumulative infiltration with time from observational data and models for the Saveh (2) and Gharehtappeh series.



Graphs 3, 4, 5 and 6. Comparison between observation and calculated (Philip model) amounts of cumulative infiltration.

Conclusion

Using the Philip model for the Saveh (2), Labar (1), Harisan (2), Gharehtappeh and Anjilavand series, including heavy to very heavy texture soils; (a) coefficient became less than zero and after time cumulative infiltration decreased. For short times (90min, 110min, and 120min) for all series except Akbarabad series, the Kostiakove and Modified Kostiakove models for determining cumulative infiltration rate, were better than the Philip model. For the Akbarabad series; Philip model shows better correlation with observations. For longer times (360min, 460min), the Philip model compares to other models in determining cumulative infiltration. For moderate times (184min, 220min, 240min) except for the following cases, conditions are similar to long times. For the Dolatabad and Labar (2) series, the Philip model is second after the Kostiakove model and for the Labar (3) series the Philip model is most suitable.

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The chemical link of forest and sea by river: materials supply from land-used soil and transport by river with reference to fulvic-Fe complex

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Abstract
In order to investigate the transport of iron-fulvic complex from forest to sea, water at 13 sites was sampled along the 88 km of Obitsu River in Chiba, Japan. The importance of the relationship between dissolved organic matter and iron (Fe) was proved. Concentrations of dissolved organic carbon (DOC) as fulvic acid and dissolved Fe in river water and surrounding soils were analyzed. In addition to investigate each major element in water, fulvic characters in DOC were analyzed by fluorescence spectrophotometer. Net production tends to decrease with increasing forest area toward midstream region and after that increasing in the downstream region. A characteristic peak of the fluorescence spectra originating from fulvic acid occurred at 440 nm with excitation 335 nm and its intensity is proportional to DOC. Concentration of DOC in soil decreased toward downstream regions, but dissolved Fe was constant. These trends indicate that abundant iron-fulvic acid complex produced in forest soil of the upstream region and forests have a greater effect on the ecosystem in the downstream region.

Key Words
Fulvic acid, iron, materials transport, land use, leaching.

Introduction
Iron is an essential element for plant growth. Iron is converted into an insoluble form because of pH change, and some recent studies suggested that dissolved iron in seawater might be limiting factor for primary production in ocean (Shibata *et al.* 2004). Fulvic acid and low molecular weight organic acids produced in forest and marsh lands are responsible for dissolving Fe from minerals in rocks or parent material in soil, and for helping to keep it soluble in water. Rivers play an important role in transport of the complex to the sea because of their source region is in mountains and they run through various lands to reach the sea. Recent research on transport of iron in Amur River has been performed as the Amur-Okhotsk Project (Shibata *et al.* 2004). Also a tree-planting program is progress in many regions in Japan which will produce fulvic acid. However, qualitative and quantitative processes of iron transport with fulvic acid from terrestrial to sea are not well understood. To gain better understanding transport mechanisms of fulvic acid from the forest to the sea, we analysed water and soil sampled along the Obitsu River using a fluorescence spectrophotometer method.

Methods
Sampling of river water and soil
Obitsu River (88 km in length and 267 km^2 in basin) is located in southern Chiba, Japan (Figure 1), it runs into Tokyo Bay and has mudland at the mouth of the river. Sampling was performed at 13 points numbered from upstream to downstream and nearby area (mudland, dry field, bamboo grove, paddy field, golf course, and forest). River water was sampled by 3 bottles (500 mL), and soil was sampled 20 cm in depth and 5cm in diameter by a polyvinyl chloride tube.

Estimating of land-use
Investigation of land use: Drainage course and integrated value of land-use area are shown in Figure 1 and Figure 2, respectively. Drainage course was analyzed by GTOPO030 and basin contribution of each water sampling point was calculated using that data. Land use was analyzed by Global Land Cover Characterization and was determined by reference to Fujii *et al.* (1987).

Analysis methods
1) River water: Current speed, river width, water depth was measured in the field. Analyzed elements in laboratory include dissolved organic carbon (DOC), total Nitrogen (T-N), phosphoric acid in the phosphorus (PO_4-P), dissolved iron (Fe), and dissolved silica (Si). In addition to evaluation of water quality, three-

dimensional fluorescence spectra of samples were obtained using a SHIMADZU RF-5300PC fluorescence spectrophotometer. The relative fluorescence intensities of the sample aliquots were reported in quinine sulfate unit (QSU) for excitation 350 nm and 455 nm using 10 μg/L quinine sulfate in 0.05M H_2SO_4. Measurement range was Ex 220~ 500 nm / Em 250 ~ 600 nm and sampling width was 5 nm. The peak of fulvic acid was determined according to *Nagao et al.* (1997).

2) Soil: Each sample from characteristic lands, which was cut into 5 cm lengths, and separated upper 5cm (0~5 cm in depth) as surface layer and lower 5 cm (15~20cm in depth) as subsoil layer. These were analyzed texture, organic matter content, and grain density. 7.0 g samples were shook with ion-exchanged water for 24 hour. The DOC and dissolved Fe in 350 mL leach liquid removed from samples were determined by SHIMADZU AA-6200 atomic absorption spectroscopy and SHIMADZU total organic carbon analyzer TOC-V_{CSH}. Major elementals were determined with X-ray fluorescence (XRF) using a RIGAKU 3491 X-ray fluorescence spectrometer.

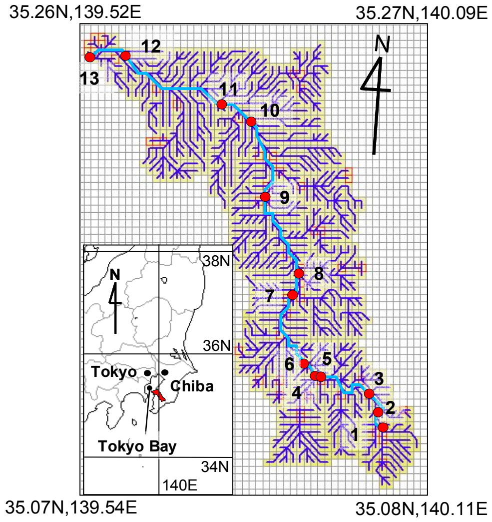

Figure 1. Sampling points (St.1~St.13) and drainage course by GTOPO030 in Obitsu river basin

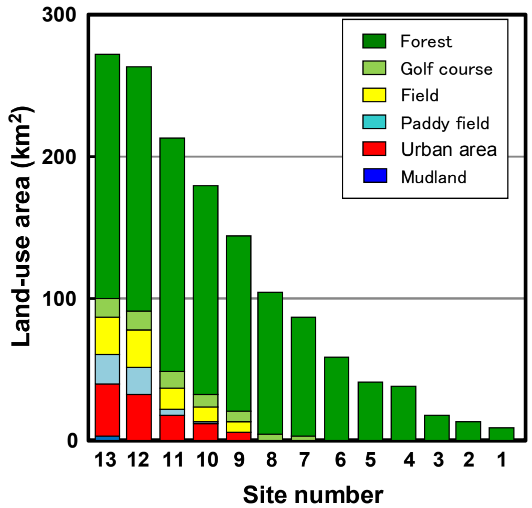

Figure 2. Integrated value of land-use area in Obitsu river basin by Global Land Cover Characterization

Results and discussions

DOC and dissolved Fe in leachate from soil

Concentration of DOC and dissolved Fe in surface and subsoil layers are shown in Figure 3. Concentrations of DOC and Fe suggested that the upstream area contributes to leaching Fe and its complex with fulvic acid. The concentration of DOC in surface soils decreased going downstream, whereas values in subsoil were unchanged except for some points. The concentration of dissolved Fe was unchanged as compared with DOC. Therefore, the ratio of dissolved Fe to DOC increased toward the downstream region, and DOC downstream had an effect on redissolution of Fe. This tendency is contrary to degree of chemical weathering or the ratio of Fe_2O_3 to SiO_2 in soil based on XRF data. This result suggests that upstream soil is likely to be weathering, but in that condition, Fe is not dissolved easily. Also, the surface layer showed higher value of

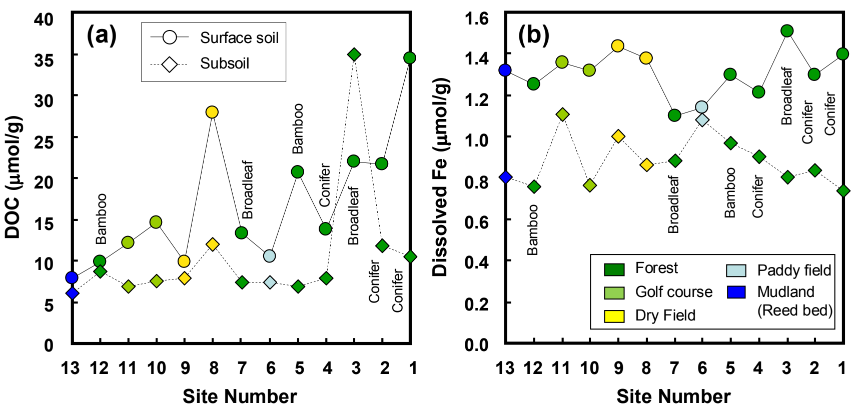

Figure 3. Concentration of DOC (a) and dissolved Fe (b) in leachate from surface and subsoil layers.

DOC than the lower layer in upstream basins, were there are conifer forest, broadleaf forest, and bamboo grove. The reason why such a sequence is found may be attributed to the facts that A-horizon may be thick under the conifer forest, and thin under the broadleaf forest. If the A-horizon is thin, organic matter is insufficient to weather the bed rock beneath, suggesting that dissolution of Fe in the broadleaf forest is more difficult than in the conifer forest. In the paddy field having a strong connection with river water, the subsoil layer showed higher values of dissolved Fe then the surface layer. It can be explained due to the fact that paddy field has oxidation and reduction layers because of separating soil from air (oxygen) by the water, Fe is soluble in the reduction layer. In fact, dissolved Fe is unchanged in both surface and lower layer but the DOC of lower layer is two-thirds as much as in the surface.

Fluorescence characterization of fulvic acid and net production

Figure 4 shows the contour plots of excitation-emission matrix (EEM) spectra for river waters at typical sampling points, and Figure 5 shows the net production of the Obitsu River basin and fluorescence intensity of fulvic acid to DOC 1 mg/L.

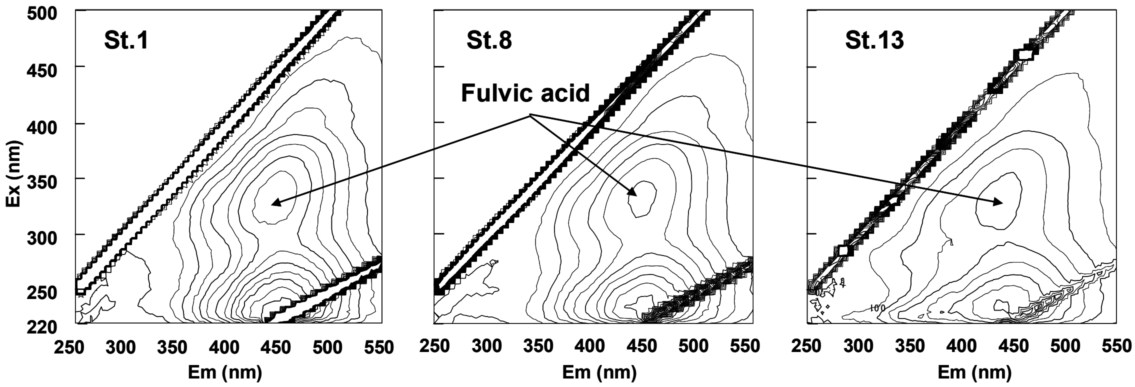

Figure 4. The contour plots of excitation-emission matrix (EEM) spectra for river waters of typical sampling points (St.1, 8, and 13).

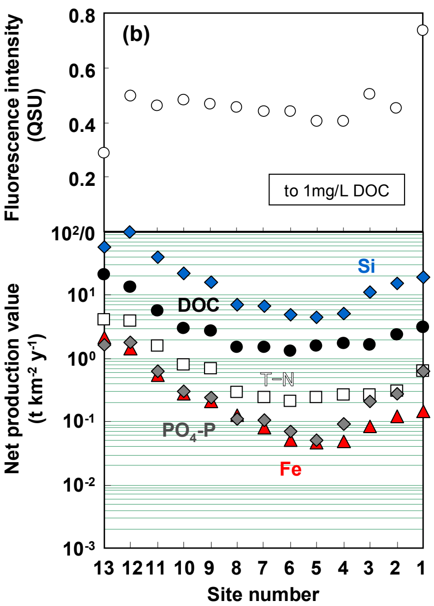

Figure 5. Net production of DOC, dissolved Fe, PO4-P, T-N and dissolved Si (a) and fluorescence intensity to 1 mg/L DOC (b) in Obitsu river water.

In fluorescence analysis, the characteristic peak originating from fulvic acid occurred at 440 nm with excitation 335 nm. Fluorescence intensity is proportional to DOC, the ratio of fulvic acid to 1 mg/L DOC is high at St. 1, the conifer forest. According to *van Hees et al.* (2005), coniferous trees supply organic acids such as citric, malonic, and oxalic acid. In most cases, forest soil produces aliphatic fulvic acid and river water produces aromatic fulvic acid. Therefore, dissolution of Fe occurs by aliphatic acid in the upstream region, and remains soluble due to aromatic fulvic acid in the downstream region.

Net production tends to decrease toward the midstream region (St. 5 or 6), and increase in the downstream region. Upstream (St. 13 to 11) and downstream regions have productivity at the same level. Dissolved Fe was expected to change similarly to DOC, T-N is unchanged similarly to DOC at midstream. This result suggests that the tendency of leaching or holding Fe is stronger than for run off from the surface in upstream region, and solution may discharge as groundwater at St. 6. Because natural gas and ancient seawater (brine water containing high concentration of fulvic acid) are mixed in the region of St. 5 and St. 6, there is a possibility that mixing of groundwater is responsible for this. In the downstream region from St. 7, net production increased with increases in other areas except for forest. Soil of the downstream region tends to have high productivity and release materials easily. At St. 13, dissolved Si and PO_4-P decreased dominantly. Dissolved Fe is also expected to decrease because of adsorption into organism living in mudland, the dilution effect or pH change mixing with sea water. It is suggested that mudland is another production region of fulvic-Fe complex.

Conclusions

(1) Net production values for fulvic acid tend to decrease as forest area increases towards the midstream region and increases in the lower river region.
(2) In fluorescence analysis, the peak of fulvic acid occurred at 440 nm with excitation at 335 nm and its intensity was proportional to DOC. The ratio of dissolved Fe to DOC in soil increased downstream and DOC downstream has an effect on re-dissolution of Fe.
(3) These results prove that abundant iron-fulvic acid complex produced in forest soil in the upstream region and forests may have a great effect on the ecosystem in the sea.

Acknowledgements

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