Effect of Activated Carbon on Risk Reduction of Persistence Organic Pollutants by Measuring Sediment-to-Water Fluxes of Polychlorinated Biphenyls

Ansara Noori (ansara.ansaranoori@wur.nl)

821215 608 070

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Abstract:

Contaminated sediment is one of the biggest concerns of many industrial areas. Previously used clean-up processes were somewhat complicated and expensive. Recently developed technique, addition of activated carbon (AC) proved its efficiency, but the eceotoxicological effects from powdered activated carbon (PAC) were sometimes ignored. In the present study, effects of different AC treatments, i.e. sediment capping with PAC, sediment amendment with GAC and sediment "stripping" with GAC, on sediment-to-water fluxes of polychlorinated biphenyls (PCBs) were studied in laboratory conditions. Effects of two bioturbators, *Asellus aquaticus* and *Lumbriculus variegatus* were considered at the same time. PAC shows maximum effect on reducing sediment-to-water flux. Flux reducing effect of stripped sediment and GAC varied from compound to compound. Less hydrophobic compounds were prompt to release from the sediment-to-water. Presences of bioturbators, highly affect the turbidity as well as increased the flux considerably. Between the two bioturbators *A. aquaticus* has the highest effect on flux whereas *L. variegatus* showed lower bioturbation activity in presence of AC.

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1. Introduction

Persistent organic pollutants (POPs) are extensively used from the explosion in industrial production [1]. They persist for long periods and easily transported by wind and water, even far from the place where they are used and released [1]. POPs come in aquatic ecosystem through effluent releases, runoff, atmospheric deposition, aerial transport, and numerous anthropogenic activities and expose threat to the aquatic system. POPs are hydrophobic, i.e. they have low water solubility; hence they bound strongly to the particulate matter in the aquatic sediment [1]. Consequently, this bound hydrophobic organic chemicals (HOCs) accumulated in to the sediment and commences long term ecological and human risk [2]. Sediment-bound contaminants may release from the sediment bed and substantially deteriorate the surface water quality. In aquatic system sediment bed is considered as a sink for many environmental pollutants including POPs. However, it becomes a potential contaminant sources when it releases the bound contaminants from sediment bed to water interface making the contaminant bioavailable for the aquatic organisms [3]. Bioavailable contaminant fraction may accumulate into the body fat of living organism, eventually, biomagnifies from one species to other through food chain. Sediment bound contaminants are a challenge to reach 'chemical and ecological status' in Water Framework Directive (WFD) which specifies environmental target [4].

The contaminated mass release from the sediment bed to water interface per unit area and per unit of time can be quantified as a flux, Φ_{sed} ($\mu g \times m^{-2} \times d^{-1}$) [2]. Flux can be measured by calculating the concentration gradients between pore water, C_p ($\mu g \times m^{-3}$) and overlying water concentration, C_{ow} ($\mu g \times m^{-3}$) and measuring the mass transfer coefficient, K_L ($m \times d^{-1}$) (eq 1)[5]:

$$\Phi_{sed} = K_L (C_p - C_{ow}) \tag{1}$$

Flux measurement can be used to assess the risk associated with the contaminated sediment since bioavailable concentration is proportional to the fluxes from the sediment bed [5]. Flux measurement can also be used to assess the effectiveness of remediation strategy [3, 5].
Release of contaminants from the sediment bed often stimulated by benthic organisms by the process of particle reworking and pore water mixing called bioturbation [4]. Likewise, non-benthic living aquatic organisms exposed to the contaminant and might uptake the contaminants from the overlying water and increase the concentration gradient between sediment and overlying water, therefore, increases the release of contaminants from the sediment that is increase the flux, Φ_{sed}.

Dredging was mostly used ex site remediation technique of contaminated sediment. Nevertheless, there are always risk from residual contaminant, destruction of benthic habitat and storage of sediment from dredging, thus it became obsolete [6]. Other mitigation process like capping with clean sediment may damage the subtle ecosystem [7].

These previously developed clean-up processes are rather expensive, laborious, time consuming and larger materials needed to be handled. A recent development of amendment in situ technique is addition of carbonaceous material (CM) like coal, char coal, black carbon. This technique is proved to reduce the bioavailability of HOC in an effective way by strengthening the sorption of toxicant to the sediment through the pore water, subsequently, lessen the toxicity of that toxicant [6-9]. Furthermore, it preserves the ecosystem and needs minimum cost and effort for application in the field.

Activated carbon, a commercially available black carbon is suitably using in this purpose. Cost effectiveness and eco-friendly characteristics of activated carbon (AC) make it more suitable for use to remediate in situ contaminated sediments and soils [10]. However, the particle size, dose, contact time and area, pore size affects the efficacy of the remediation technique with AC [6, 8, 11]. Powered and granulated forms are two most commonly available variety of AC [12]. According to Zimmerman et al. [11] the sorption activity of AC has negative relation with the particle size of the AC. Having larger surface area, and lower particle size, powered activated carbon (PAC) is chemically more efficient sorbent compare to granular activated carbon (GAC). Because of this superior sorption action and kinetics powdered activated carbon (PAC) is more frequently used to reduce sediment-to-water contaminants release [13].

Notwithstanding, PAC is doubting as long life element [14]. It could not be removed from the sediment after remedial activities and residual PAC may come in the body of benthic organisms with food and disturb the habitual behaviour. It was proved that presence of carbonaceous material in sediment causes reduction of body fat and the habitat quality loss in contrast to clean sediment [9]. Jonker et al [15] has reported numerous ecotoxicological effect of AC addition to sediments and according to Cornelissen et al [16] these effects are suspected to amplify with time. However, the long term effect of PAC on sediment ecosystem is yet unknown[10] because of the infancy of this technique [10]. Thus, despite many advantages, PAC might have significant negative effect including the abundance, richness, quality and biodiversity of benthic community [16, 17].

Though GAC is not as efficient sorbent as PAC but GAC could be more economical choice in contrast to PAC, since, it has little chance of loss and is easily manageable. On the contrary, PAC is difficult to manage since it forms dust and during placement a percentage of it may loss which induces greater operating cost per square meter sediment [16]. Moreover after application GAC may be removed from the sediment bed effortlessly and could be regenerated for further use. Consequently, GAC may have no possibility of long run effect on benthic organisms. On the other hand, PAC cannot be reused and it produces huge amount of sludge as well which are difficult to manage.

Taking all these facts in to account, in this study, both PAC and GAC were used to mitigate the risk associated with contaminated sediments, purpose is to introduce GAC as sorbent material for the sediment bounded contaminated and test its efficacy. The remediation

performances of both sorbent materials (PAC and GAC) were assessed by measuring the sediment-to-water fluxes of one group of POPs, polychlorinated biphenyls (PCBs) which is found in alarming concentration in many water bodies over the world [8]. The measured fluxes in presence of sorbent materials were compared without sorbent material (control) as well. Besides, the presence of benthic and non-benthic organisms was also considered in flux measurement and to distinguish their interfering effect, the release of contaminants with and without organisms was measured. For this experiment two fresh water sediment dwelling species one macro invertebrate and a black worm were selected, both of these act as turbicid. The choice for macro invertebrate was an isopode *Asellus aquaticus* and an oligochaeta *Lumbriculus variegatus* (black worm)**.** The reasons behind choosing *A. aquaticus* was their availability and sensitivity towards hydrophobic organic pollutants [18] and *L. variegatus* black worm was chosen as benthic organism (turbicid) because of their culturing simplicity.

Objectives

The current study had several major goals:

1) Evaluate the effect of different AC (both PAC and GAC) treatments on the sediment-to-water fluxes of sediment bound HOCs.

2) Compare the effectiveness of PAC vs. GAC as sorption material for PCBs.

3) Measure the interfering effect of two benthic macro invertebrates on sediment-to-water fluxes in different AC treatments.

This study was based on laboratory sediment-to-water flux measurement. It was done by measuring the amount of desorbed contaminants from the sediment using Empore disks as a sink for PCBs in the overlying water. The measurements were taken in different time points with and without organisms and the effectiveness of both AC were characterized by comparing the amount removed in different treatments.

2. Materials and Methods

2.1 Chemicals and materials

In this experiment all water used was Barnstead Nanopure water (Sybron-Barnstead, Dubuque, IA, USA).

PCBs standards

The PCBs standards 2,2',5-trichlorobiphenyl (CB18), 2,3,3'-trichlorobiphenyl (CB 20), 2,4,4'-trichlorobiphenyl (CB28), 2,4,5-trichlorobiphenyl (CB 29), 2,4',5-trichlorobiphenyl (CB 31), 2,2',3,5'-tetrachlorobiphenyl (CB44), 2',5,5'-tetrachlorobiphenyl (CB52), 2,2',4,5,5'-pentachlorobiphenyl (CB101), 2,3,3',4,4'-pentachlorobiphenyl (CB 105), 2,3',4',4,5-pentachlorobiphenyl (CB118), 2,2',3,4,4',5'- hexachlorobiphenyl (CB138), 2,2',3,4,5,6'-hexachlorobiphenyl (CB143), 2,2',3,4',5',6-hexachlorobiphenyl (CB 149), 2,2',4,4',5,5'-hexachlorobiphenyl (PCB153), 2,2',4,4',6,6'-hexachlorobiphenyl (CB 155), 2,2',3,3',4,4',5-heptachlorobiphenyl (CB170), 2,2',3,4,4',5,5'-heptachlorobiphenyl (CB180), 2,2',3,3',4,4',5,5'-octachlorobiphenyl (CB 194), 2,2',3,4,4',5,6,6'-octachlorobiphenyl (CB 204) and 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl (PCB209) were obtained from Promochem (Wesel, Germany). 2,3',5,5'-tetrachlorobiphenyl (PCB72) was obtained from Ultra Scientific (North Kingstown, RI, USA).

PAHs standards

The PAHs standards phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*e*]- pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo-[*a*]pyrene, benzo[*g,h,i*]perylene, dB(ah)anthracene, naphthalene and ind(123)pyrelene were obtained from Sigma-Aldrich or Acros Organics, The Netherlands, and all had a purity of more than 98%. The Community Bureau of Reference (BCR), Geel, Belgium was supplied the internal standard 2-methylchrysene with 99.2% purity.

Other chemicals

 Picograde quality organic solvents hexane and acetone (Promochem; picograde), methanol (Mallinckrodt Baker, Deventer, The Netherlands; HPLC gradient grade), acetonitrile (Lab-Scan, Dublin, Ireland; HPLC grade), 2,2,4-trimethylpentane (Mallinckrodt Baker, Deventer, The Netherlands), 37% concentrated hydrochloric acid (HCl) (Sigma-Aldrich, Germany), sodium sulphate (Na_2SO_4) (Merck, Darmstadt, Germany), aluminium oxide (Al_2O_3) (Super I; ICN Biomedicals, Eschwege, Germany), silica gel 60 (Merck, Darmstadt, Germany; 70-230 mesh), copper powder (99.7%; Merck), and Empore™ discs (47 mm; J.T. Baker, The Netherlands). The Empore disks were composed of an octadecylsilica (C_{18}) phase immobilized on poly tetra fluoroethylene (PTFE) fibrils, extraction sheaths made of glass fibre (33x94 mm, Schleicher & Schuell), boiling stones.

Before using, silica gel was activated overnight at 180 °C, aluminium oxide was deactivated with 10% (w/w) Barnstead Nanopure water, to remove the water, contaminants and organic materials, sodium sulphate (Na_2SO_4) was dried in the muffle furnace at 550 °C, copper powder and boiling stones were Soxhlet-extracted with hexane for 4 h, and Empore disks were cleaned with 10 ml methanol using a vacuum filter after which they were air dried, glass fibre extraction sheaths were Soxhlet-extracted with 160 ml of a 1:3 acetone/ hexane mixture for 1 hour.

Lab apparatus and accessories

Other apparatus and accessories used were capper for krimpcap vials, desiccator, rack for evaporation with nitrogen, columns– white and amber colored, rack for columns, kuderna-Danisch evaporation-equipment–modified (6x), sterile Quartz wool (Varian), glass cylinders 100 ml and 25 ml (3x), muffle furnace (up to 1000° C: Thermolyne Model F-A1730 equipped with an auxiliary temperature controller Thermolyne Furnatrol 133, Sybron Corp., Dubuque, IA), EA 11100 CHN elemental analyzer (CE Instruments, Milan, Italy), mortar stamper, parafilm, Pasteur pipettes (long) with suction tool (rubber balloon), petri dishes, flat bottom flask 250 ml, porcelain cups for dry matter measurements (30x), porcelain dish, point flask 100 and 250 ml both white colored (24x) and amber colored (12x), standard laboratory set of glasses and tools like Erlenmeyer (conical) flasks, beakers, flasks, tweezers, scissors and spatulas, socorex pipet 0.5–5 ml, Soxhlet extraction equipment:100 ml extractors and Dimroth coolers, ultrasonic vibration bath, vials both amber colored and transparent with matching caps (red and white septum), rack for vials, vortex, water baths with 6 holes, reaching 120°C, turbidity meter (Aquafluor, Turner Designer, Sunny vale, CA, USA), accelerated solvent extractor (ASE 350, Dionex, USA) with 28 samples extraction capacity, electrical microbalance (Cahn 25 Automatic Electro balance; Ventron Corp., Cerritos, CA), small silver cups both short (8×5mm) and long (12.5×5 mm) (Elemental Microanalysis Limited, UK). Besides, 1.5 mm mesh Stainless steel (SS) wire mesh was used to make the cages for Empore disks (ED) and SS thin rods were used to make the hooks for hanging the cages.

Activated Carbon

Both powdered activated carbon (PAC) and granular activated carbon (GAC) were obtained from Norit Activated carbon, Amersfoort, The Netherlands. PAC used was virgin powdered coal-based Norit SAE Super (particle size 1-150 µm). NORIT GAC 1240W which was produced by steam activation of coal was used in this experiment [30]. Particle size of GAC was between 12 and 40 meshes (0.425 - 1.70 mm) and had superior hardness.

Organisms

Asellus aquaticus was collected from clean Duno pond in Doorwerth, The Netherlands, using a sampling bucket. Organisms, were transferred to the laboratory, sorted to get a group of organisms with a size range 4-7 mm, and kept in aerated copper free water in white bucket in a climate-controlled room at 18°C. Organisms were fed dry poplar leaves collected in the field. *Lumbriculus variegates*, cultivated in house, and was kept in reared glass aquaria at 18 °C. Chlorine-free cellulose served as substrate, and the aquaria were continuously flushed with copper free water. Once a week, the organisms were fed with pulverized flake fish food.

Sediment

The sediment used in this study was dredged from Biesbosch national Park lake Netherlands. This sediment was inherently contaminated with POPs, mainly PCBs and PAHs. Before using in the experimental ditches the sediment was homogenized for 24 h on site, and diluted to 20% d.w.

2.2 Experimental set up

The dredged material was transported to the experimental facility Sinderhoeve, Renkum, The Netherlands, where four rectangular identical artificial ditches (15 m length × 2 m width on the top × 1.5 m width on the bottom × 1 meter depth) were prepared prior the experiment. The first ditch was filled with homogenized sediment to create 10 cm layer (control system). The second ditch was filled with the sediment in the same manner, and then the sediment was capped with PAC to achieve 4% d.w. PAC in the top (bioactive) layer (upper 10 cm) of the sediment. The sediment for the next treatment was mixed with 4% GAC, homogenized for 24 h, and then placed in the third ditch. Finally, the rest of the sediment was mixed with 4% GAC, homogenized for 48 h, after which GAC was sieved out using 1 mm sieve, and the forth ditch was filled with this "stripped" sediment. The ditches were filled with water. The sediment in all ditches was allowed to settle down for four days before sampling. The schemes of treatments ditches (see in appendix 1, fig: 1.1 and 1.1) were:

Ditch 1	Ditch 2	Ditch3	Ditch4
Homogenized sediment	Homogenized sediment	Homogenized sediment	Homogenized stripped sediment
No sorbent material	4% Norit PAC	4% Norit GAC 1240W	GAC sieved out
water	water	water	water

2.3 Sediment sampling and pre-treatment

A representative mixed sample was taken from each ditch using a PVC core (5cm in diameter) sampler and on the same day transported to the laboratory. The mixed sediment samples were homogenized with an electrical stirrer for 10 min, after which the sediment was diluted with water from the corresponding ditch to achieve L/S comparable to the one in the ditch, i.e. 5. The obtained slurry was homogenized mechanically and then divided in four equal subsamples using the slurry distributor. One subsample was used for the survival experiment and the other three for flux experiment. After distribution the samples were transferred to 2.5 L brown colored bottles. Bottles were shaken horizontally (120 rpm) at room temperature for 28 d.

2.4 Flux experiment

After 28 days, the samples were transferred to 12 PVC cylindrical cores (three cores per AC treatment) having 60 cm height and 6 cm inner diameter. The sediment in all cores was allowed to settle down for 1 week prior the experiment. After settling period, 10 individuals of *Lumbriculus variegatus* were added to each of four AC treatment cores and 10 individuals of *A. aquaticus* were added to another four cores (see in appendix 2, fig: 2). Two Empore disks in a stainless steel cages inserted in each core were positioned at a distance of 10 cm from the sediment surface. Stirring of the disks was adjusted to the highest possible rate before sediment resupension occurred (36 rpm). Empore disks (ED) were placed in the overlying water at incremental time intervals after 0.17 (4 h), 1, 2, 7, and 14 d.

Empore disk extraction, clean-up, and analysis

The EDs were extracted twice with 20 ml methanol using ASE. Extraction was done at 70 ^{o} C and high pressure which required half an hours per sample. The extracts were collected in glass tubes, cleaned and then analyzed for PAHs and PCBs following the same procedure as in 2.5.2.

2.5   Turbidity measurements

The turbidity in every core was measured on a weekly basis using a simple turbidity meter which works with UV light absorbance. Small portion of water (1-2 ml) was taken from each core from the same depth (10 cm from the top water level) using a long pasteur pipet and transferred to a cuvette. Once the turbidity was measured the water was restored to the system.

2.6 Sediment analysis

2.6.1 Black carbon and total organic carbon (BC/TOC) analysis

Total organic carbon (TOC) and black carbon (BC) were measured in triplicate using the chemothermal oxidation method (CTO375) with an EA 1110 CHN elemental analyser [5]. The process was divided in to three parts: 1) sample preparation 2) removal of inorganic carbon

(IC) from the dried ground sample by acidification 3) quantification of residual carbon as BC using CHN elemental analyser.

The samples were prepared by drying overnight at 105° C and 375° C which followed grinding. The inorganic carbon was removed by acidifying small amount ground sediment with 2M HCl and water repeatedly (25 µl of H_2O, 25 µl and 50 µl of 2M HCl successively) [19]. The resulting pre-treated samples were analyzed for BC and TOC in EA 1110 CHN elemental analyser equipped with a GC detector. In the CHN analyser the samples were first oxidized in the column packed with chromium oxide (Cr_2O_3) where flow of oxygen was used to associate the oxidation process. The columns were washed with the flow of helium (He) gas. The oxidation was taken place at 1000°C. A couple of calibration (atropine) and reference samples were also analysed with the sediment samples for assurance the quality of the measurement.

2.6.2 Determination of PCBs concentration in the contaminated sediment

To measure the PCBs concentration in sediment, the sample was prepared by grinding 1 g d.w. with Na_2SO_4 (1:3 w/w). Sediment samples were Soxhlet-extracted with 160 ml of a 3:1 hexane and acetone (v/v) for 16 hours. After overnight extraction, the extracts were cleaned over Al_2O_3 and splitted in two portions for PAH and PCB analysis. PCB fraction was cleaned over the SiO_2 columns and then the samples were desulfurized using Cu powder in the ultrasonic bath and spiked with IS (CB-143). Concentration of 19 PCBs congener were measured using a Hewlett-Packard 5890 series II Gas Chromatographer (GC) which was equipped with a 7673 auto sampler, two "63Ni Electron Capture Detectors" and two capillair "fused silica" columns (CP Sil-8 CB and CP Sil-5 CB). For each sample the injection volume was 20 µl and mobile phase was nitrogen.

PAH fraction was spiked with internal standard (3-methylchrysene) and PAHs were analysed using a Hewlett-Packard 1100 High Performance Liquid Chromatographer (HPLC) equipped with a multi wave length fluorescent detector, analytic C18 reversed phase columns (201TP54) guard with Vydac (201GD54T). Here, methanol and water was used as mobile phase, injection volume of the sample was 20 µL per sample.

A couple of PAH and PCB standards were run with the samples in the beginning, middle and at the end of the sample series.

Quality assurance and quality control

For quality assurance multiple blank and recovery determinations were done for Empore™ disk as well as for the sediment and the obtained data were corrected for the resulting values. The recoveries were prepared by spiking 200 µl of the recovery standard to the ED and dried the solvent by socking it with tissue paper. Blank PAHs and PCBs concentrations were negligible compared to sample extracts and the recoveries were considered as 100% sample extract.

2.6 Survival experiment

Survival of *A. aquaticus* and *L. variegatus* exposed to control, PAC, GAC, and "stripped" sediment was tested by adding 10 individuals to beakers with 1 cm wet sediment and 200 ml (for *A. aquaticus*) and 50 ml (for *L. variegatus*) copper-free water. The beakers were aerated and *A. aquaticus* were fed dry poplar leaves over a 21-d period. For *L. variegatus* the period was 28-d. The experiment was performed in triplicate in a climate-controlled room at 18°C and 12:12 light:dark cycle. Survival was determined by gently transferring the beaker content to a tray and counting living organisms.

3 Results and discussions

3.5 Sediment analysis

The characteristics of the Biesbosch sediment used in this experiment are summarized in table 1. Total concentration of 14 different PAHs was 11.36 mg/kg ds. This value is 10 times higher than the new listed optimum concentration in Dutch standard guidelines [31]. Among these 14 PAHs fluoranthene (FLU) is the dominant PAH in this sediment (see in figure 1 A), followed by cryrene (CYR), benzo[a]anthracene (B(a)ANT), benzo[a]-Pyrene (B(a)PYR), and bezo[k]fluoranthene (B(k)FLU). The reason behind the most dominated compound as FLU, CRY, B(a)ANT, B(a)PYR is their 4 and 5 rings characteristics in their structure. This result consistence with the highest persistency shown in 4-6 ring congener among all PAHs congener, with subsequent highest abundances [21].

PAH concentration ratios PHE/ANT and FLU/PYR in the Biesbosh sediment were 1.26 and 11.19, characterizing PAH contamination as of pyrolytic origin since PHE/ANT<10 and the FLU/PYR>1 indicates the pyrolytic orgins of PAHs [21]. Besides, other ratios like ANT/178, FLU/(FLU + PYR), BaA/228 and InP/(InP + BghiP) are also shown in table 1, gives the identification of pryrogenic origin of this sediment which comes from kerosene, grass, most coal and wood combustion samples and creosote sources [7]

The total concentration of 7 PCBs congener was found to be 0.45 mg/kg ds. This value exceed the optimum concentration in Dutch new standard list, 2012 which is 0.02 mg/kg [31]. In terms of individual congener, the predominant congeners were CB 153, CB 52 and CB 101 (see in figure 1 B). However, all of the 7 congeners were found distributed in Biesbosch sediment. The heavy metals content in the sediment are listed in table 1. All of them are above the optimum level of Dutch new standard list [31]. Zinc is the most abounded metal in Biesbosch sediment. Besides, other 7 toxic heavy metals like arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pd), nickel (Ni) were also found to some extent in this sediment.

Total organic carbon and black carbon content were 5.86 and 1.15%, respectively (see in table 1).

Table 1. Geochemical characteristics of the Biesbosch sediment

PAHs	Csed, mg/kg	Ratios of PAHs	values	Inorganic parameters	
Phenanthrene (PHE)	1.10	PHE/ANT	1.26	**Metals**	**in mg/kg ds**
Anthracene (ANT)	0.87	FLU/PYR	11.19	Arsenic (As)	50
Fluoranthene (FLU)	2.20	ANT/178	0.00	Cadmium (Cd)	6.5
Pyreen (PYR)	0.20	FLU/(FLU + PYR),	0.92	Chromium (Cr)	190
B(a)Anthracene B(a)ANT	1.20	BaA/228	0.01	Copper (Cu)	120
Chryseen(CRY)	1.40	InP/(InP + BghiP)	0.45	Mercury (Hg)	5.1
B(e)Pyreen B(e)PYR	0.13	ANT/ANT+PHE	0.44	Lead (Pd)	170
B(b)Fluoranthene B(b)FLU	0.19	**PCBs**	**mg/kg ds**	Nickel (Ni)	26
B(k)Fluoranthene B(k)FLU	1.00	CB 028	0.06	Zinc (Zn)	920

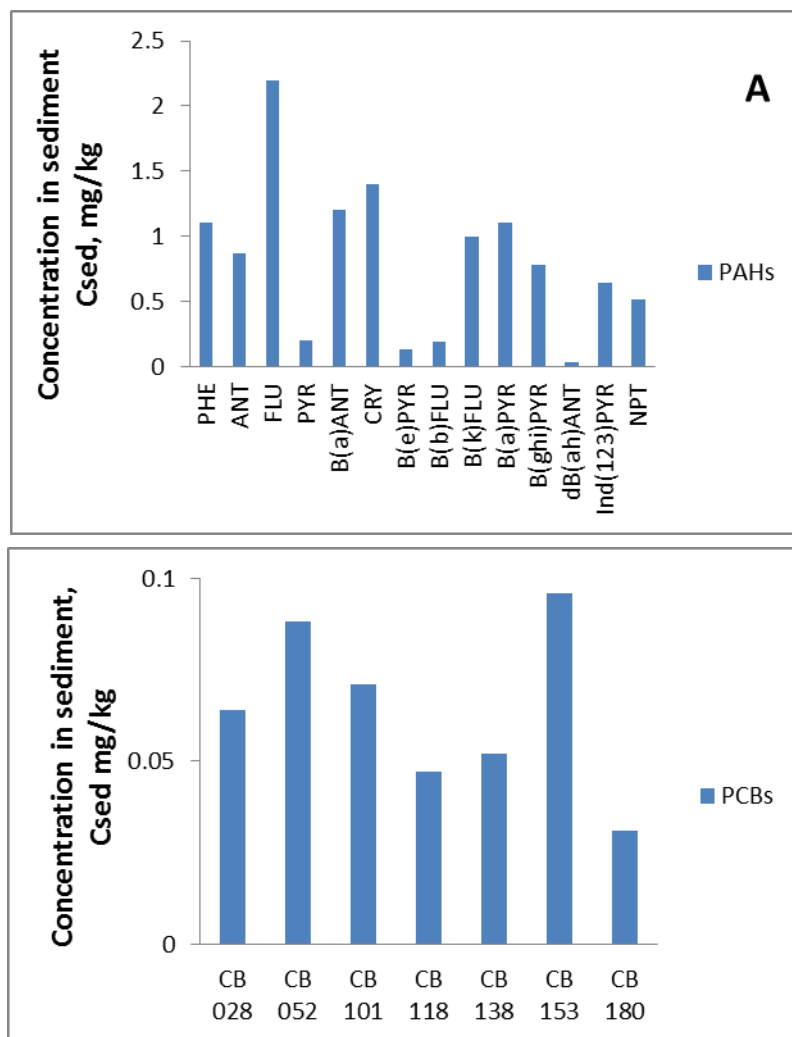|				Organic parameters	%
B(a)Pyreen B(a)PYR	1.10	CB 052	0.09	**Organic parameters**	**%**
B(ghi)Perylene B(ghi)PYR	0.78	CB 101	0.07	Black carbon (BC)	1.15
dB(ah)Anthracene dB(ah)ANT	0.03	CB 118	0.05	Total Organic Carbon (OC)	5.86
Ind(123)Pyreen Ind(123)PYR	0.64	CB 138	0.05	Amorphous OC (AOC)	4. 71
Napthalene (NPT)	0.51	CB 153	0.10	organic matter (OM)	6.8
		CB 180	0.03		
∑ PAHs	**11.36**	**∑ PCBs**	**0.45**		

Figure 1. The concentration of individual PAHs (A) and PCB congener (B) in the Biesbosch sediment

3.6 Survival experiment

After 3 weeks exposure in four different AC treatments (control, PAC, GAC, stripped) the lowest survival of *A. aquaticus* (see in figure 2) was found in control and the highest in PAC treated sediment (see in figure 4). Moreover the survival in stripped sediment is lower compared to GAC treated sediment. This result indicates that AC (both PAC and GAC) increases the survival of *A. aquaticus* in the contaminated sediment due to the attenuation of bioavailable contaminants. In general, mortality of *A. aquaticus* was very high in all systems (except in the PAC) which reveal that the exposure level of contaminants might be above the 50% lethal concentration (LC_{50}) for this species.

No mortality of *L. variegatus* was found after 4 week exposure period in this experiment. The highest survival was found in the PAC treated sediment and the lowest in the control. Same as *A. aquaticus*, the survival of *L. variegatus* was higher in the sediment amended with GAC than in the stripped sediment. No mortality of *L. variegatus* illustrates the reproduction of this species as well as the contaminants level was may not be exceeded the LC_{50} of the contaminants for *L. variegatus.*

Between the two turbicid, *A. aquaticus* exhibited higher sensitivity towards the contaminated sediment in all systems showing lower survival percentage. According to De Lange et al, 2000 [26] *A. aquaticus* is highly sensitivity towards HOCs and tries to circumvent it. In all replicates lots of juvenile *A. aquaticus* were found and more than 100% survival of *L. variegates* were observed which were the evidence of reproduction of both species.

Figure 2 *Aselluse aquaticus (www.naturfoto.cz)*

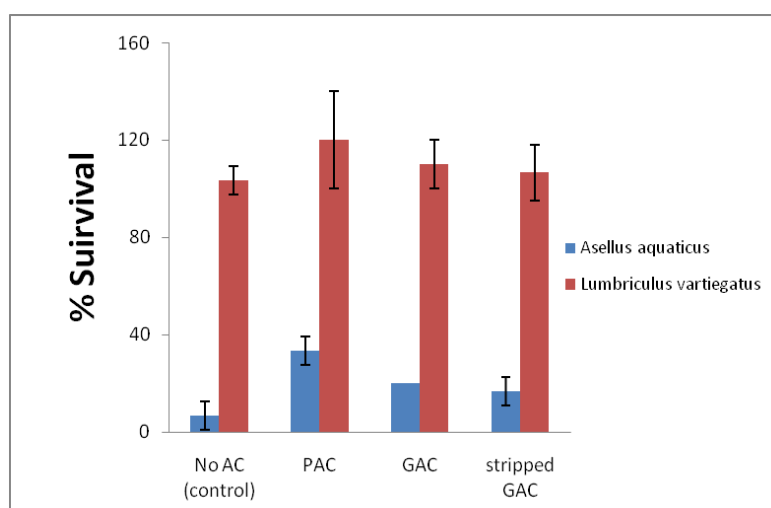**Figure 3** *Limbriculus vartiegatus (www.biopix.com)*

Figure 4 Survival of *A. aquaticus* and *L. variegates* after 21-d exposure to the Biesbosch sediment capped with PAC, amended with GAC, and stipped with GAC.

Toxic effect of a contaminant depends on its uptake by the organisms which could be predicted from the bioaccumulation concentration [27]. Addition of AC in contaminated sediment reduces the bioavailability of HOCs, eventually reduces the toxic effect [11,15, 28]. In actual case AC gives its effect best after 4 weeks of its application [14]. In this experiment the sediment was used immediately after 1 week of AC application which is not sufficient time to achieve the maximum effect of AC on reduction of bioavailable concentration. Despite this fact, PAC itself may impose toxic effect towards *A. aquatisus and L. variegatus.* However, this effect is not observed when PAC is treated before application [15, 29]. Conversely, according to Jonker *et al, 2009* [15] the untreated PAC might have a negative effect towards *L. variegatus* survival in concentrations above LC_{50}. Even though untreated PAC was used in this experiment, the dose was only 4% of the sediment which may be lower than LC_{50} as well as the exposure time was too short to cause the toxic effect. Thus only the

positive effect of AC was observed. Again the mortality and reproduction are not always the most sensitive endpoints [26]. Though in all systems and replicates at least certain survivals of *A. aquaticus* were found, however, survived individuals of *A. aquaticus* did not behave as healthy organisms, they were a bit indolent in their movement. This alternation in motility may vary by gender, individual body size, feeding state and presence of contaminants as well [18].

3.3 Turbidity measurement

The results of turbidity measurements overtime are given in the table 4 (also seen in Figure 5). It was observed that the turbidity varies from treatment to treatment, however, the highest turbidity levels were found in treatments (except control) with *A. aquaticus*. With *L. variegatus* the highest turbidity was observed in control, followed by other three AC treatments (GAC, PAC and stripped sediment) (see in figure 6 and appendix. 4 table: 4)

In the control treatment (no AC) the highest turbidity was observed in the presence of *L. variegatus*. However, in the PAC treated sediment the turbidity in the system with no organisms was higher than in the system with *L. variegatus* which may be due to the re-suspension of

Control (No AC)

PAC

GAC

Stripped Sediment

No Organism   Lumbriculus   Asellus

Figure 5 Visual variations in turbidity in different treatments

lighter PAC particle in absence of organisms by the rotating cage of ED. The lowest turbidity was observed in all non-bioturbated treatment (except the PAC treated sediment). In the absence of organisms no mechanical transport and resuspension of sediment particle from the sediment to the overlying water occurred which leads to a decrease in observed turbidity.

Unlike AC treatments, in control (no AC), turbidity in the presence of *A. aquaticus* was lower that in the system with *L. variegates* which was consistent with the results of the survival experiment. In the survival experiment the highest mortality of *A. aquaticus* was found in control thus with reduced number of organisms over time, decreased turbidity was observed.
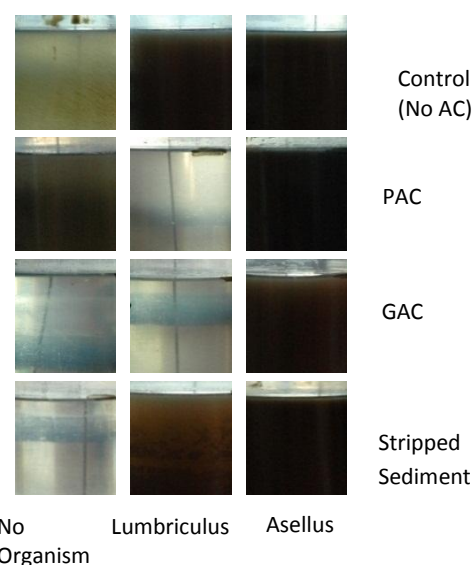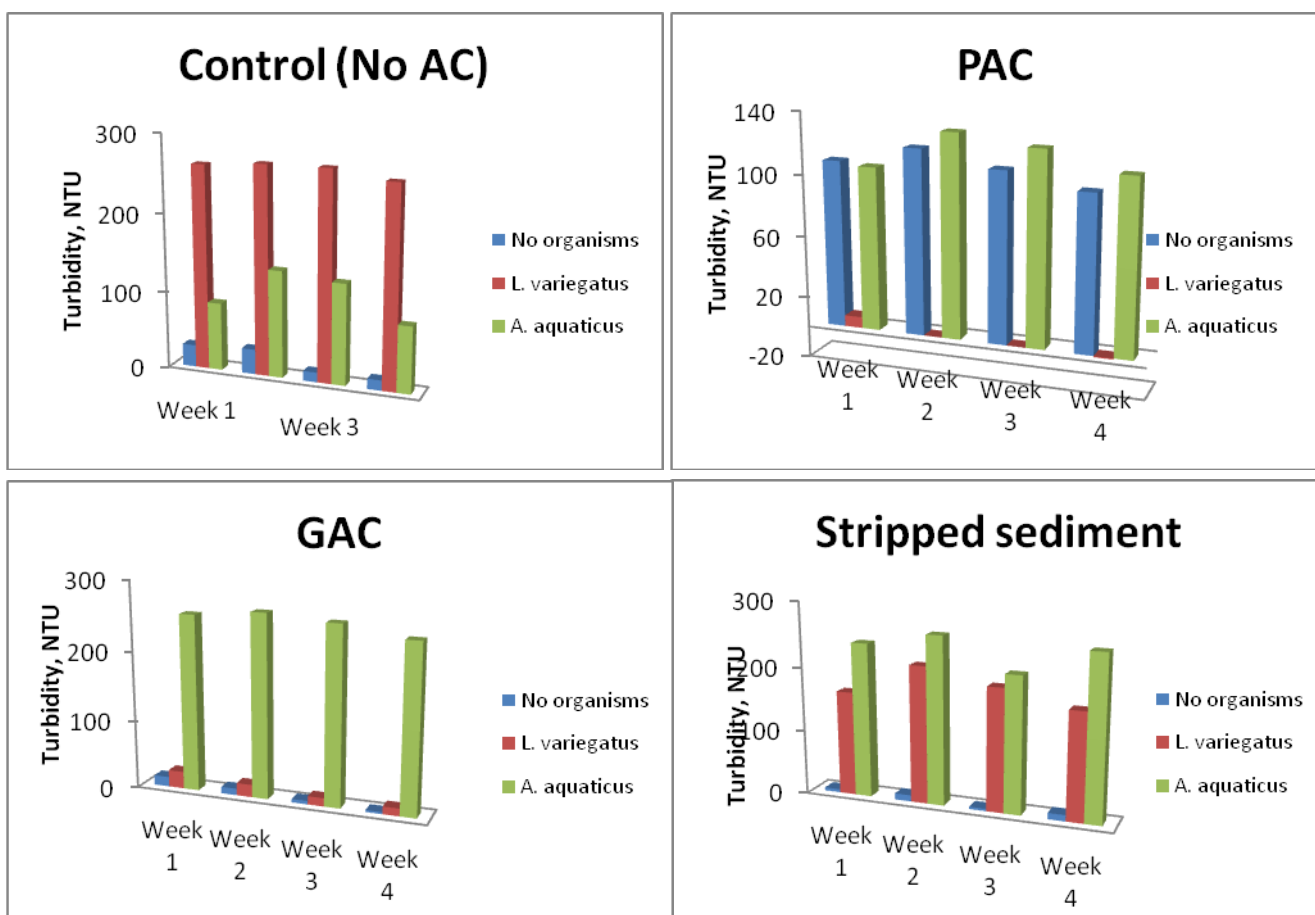
Figure 6 Turbidity in different AC treatments in the presence and absence of bioturbators

In the systems with *L. variegatus* turbidity drastically decreased in the presences of AC. Since a high survival of *L. variegates* was observed in the AC treatments, decreased turbidity cannot be attributed to mortality in these systems. However, the effects of AC on other endpoints, e.g. reduced egestion rate and lipid content, of *L. variegatus* have been reported previously (Jonker 2004, 2009) that could have an effect bioturbation activity of the species. Moreover, reduced bioturbation activity of fresh water benthic worm has recently been reported in the presence of BC (Koelmans 2011). In this experiment turbidity increased in absence of AC in stripped sediment *with L. variegatus.* Because, in stripped sediment there expected little or no residual AC to execute chromic toxic effect of AC towards the worm to reduce the bioturbation activity.

The observed differences in bioturbation activity of *A. aquaticus* and *L. variegatus* could originate from the vertical distribution of resting stages [7, 30]. *A. aquaticus* resides on the sediment surface, moves actively around the sediment and cause major bioturbation by mechanically disturbing the whole sediment surface, whereas, *L. variegatus* resides in the sediment and cause intermittent bioturbation.

Oxygenation is another bioturbation stimulus which boosts up mineralisation process and makes the release of nutrient from the sediment to the overlying water [7]. Accordingly due to the consumption of oxygen by the sediment dwelling organisms, consequences lighten

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the turbidity with time. Moreover, there was no external food or nutrient supply in the system (because external food suspected to complicate the interpretation of the results) and the enduring nutrients may uptake by the organisms which eventually consumed within the experimental exposure time. Thus diminution of the nutrient in the system might cause reduction of the turbificid activities with subsequence attenuation of the turbidity. In control there were no oxygen consumption in absence of organisms, though, as time pass the turbidity should decrease. This might be because of the better settlement of the sediment particles due to gravity and chemical binding of the sediment surface with times. Nevertheless, the time expanse of this experiment was not that much to decrease the turbidity remarkably.

3.4 Flux experiment

A total of 19 PCBs were detected and quantified in the flux experiment. Three representative PCB, i.e. CB-52, 138, and 204, were selected to study the effect of AC treatments as well as bioturbation activity on the sediment-to-water fluxes of PCBs.

For CB-52 which is a tetrachlorinated biphenyl, the highest mass extracted by the ED was found in control treatment (no activated carbon) all through the systems (without organisms, with *A. aquaticus* and with *L. veriegatus*) (see in figure 7). However, in absences of organism the lowest removed CB-52 by the ED was observed in stripped sediment, where, in presences of both organisms the lowest mass extracted by the ED was in PAC treated sediment. Thus PAC was proved as the most effective sorbent in presence of both bioturbators. Nevertheless, the second highest extracted mass in presence of *A. aquaticus* was observed in GAC treated sediment, whereas, in presence of *L. variegates* stripped sediment found more effective than GAC treated sediment.

In presence of bioturbators the amount of extracted CB-52 was much higher than without organisms. With *A. aquaticus* the removed amount of CB 52 was 4.5 times higher than without organisms and with *L. veriegatus* it was nearly 2 times higher in contrast with no organism system (see in figure 7). Thus it could be said that presences of bioturbators help the easier release of contaminants from the sediment.
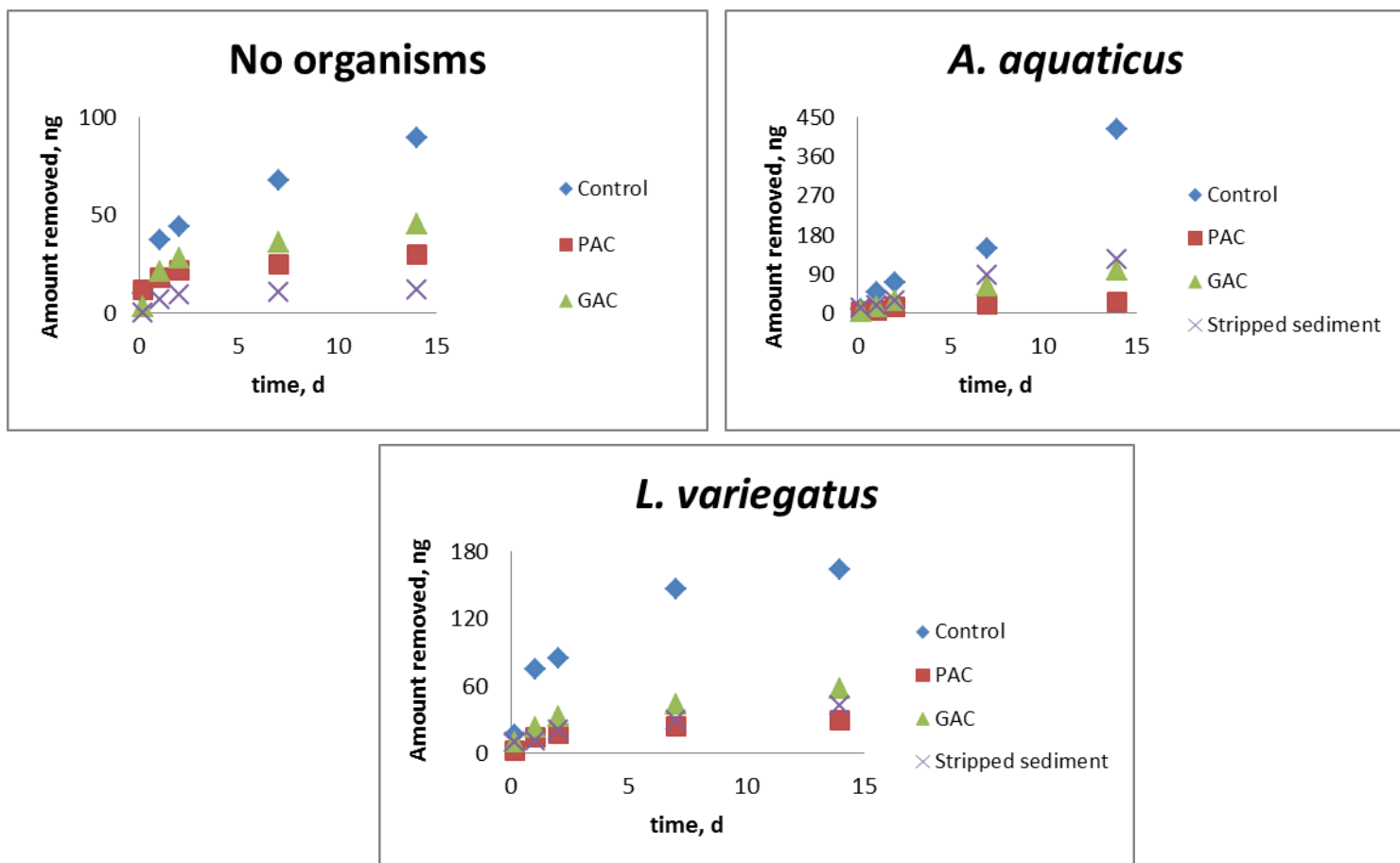
Figure 7 Measured extracted mass of CB-52 from overlying water using Empore disks, for non-bioturbated system (A) and systems with *A. aquaticus* (B) and *L. variegatus* (C) in different AC treatments.

In case of hexachlorinated biphenyls, CB-138, irrespective to the system, we observed the highest extracted amount in control treatment (with no AC) and lowest amount in the PAC treated sediment (see in figure 8). Thus PAC was found the most effective sorbent for CB-138. Stripped sediment was found as the second most effective treatment where there were no organisms, but GAC shown its more effectiveness than stripped sediment in presences of bioturbators. Same as CB-52 the amount of CB-138 removed by the ED was also higher in presence of bioturbators than in absences of bioturbators. And with *A. aquaticus* the extracted mass was more than 3 times higher and with *L. variegatus* it was 3 times higher than without organisms (see in fig. 8). Furthermore, it was observed that, the maximum amount of extracted CB-138 was quite lower than the tetrachlorinated biphenyl, CB-52 in the respective treatment and same exposure time.
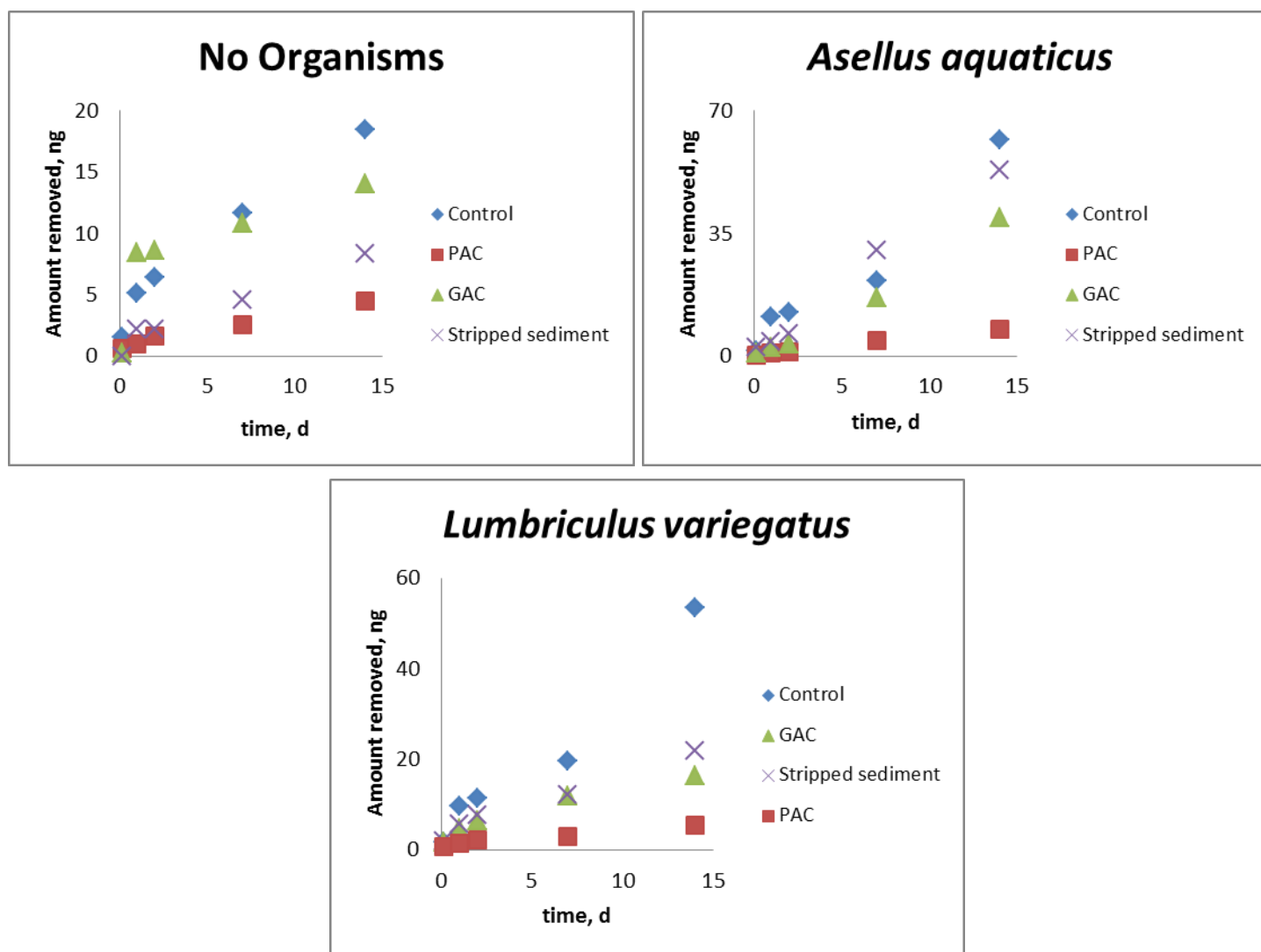
16

Figure 8 Measured extracted mass of CB-138 from overlying water using Empore disks, for non-bioturbated system (A) and systems with *A. aquaticus* (B) and *L. variegatus* (C) in different AC treatments.

The extracted amount of octachlorinated biphenyls, CB-204 was found quite little with respect to the other PCBs (see in fig 9) regardless with system. However PAC treated sediment released lowest CB-204 in absences of bioturbators and in presences of *A. aquaticus*, whereas, in presences of *L. veriegatus* the GAC treated sediment released lowest amount of this PCBs. Similar with other PCBs, the highest extracted amount was found in control treatment (no AC). In presences of both bioturbators the released amount of CB-204 was higher than without organisms and the highest amount was removed in presences of *A. aquaticus* which is 5 times higher than without organisms and almost double than in presences of *L. veriegatus*.
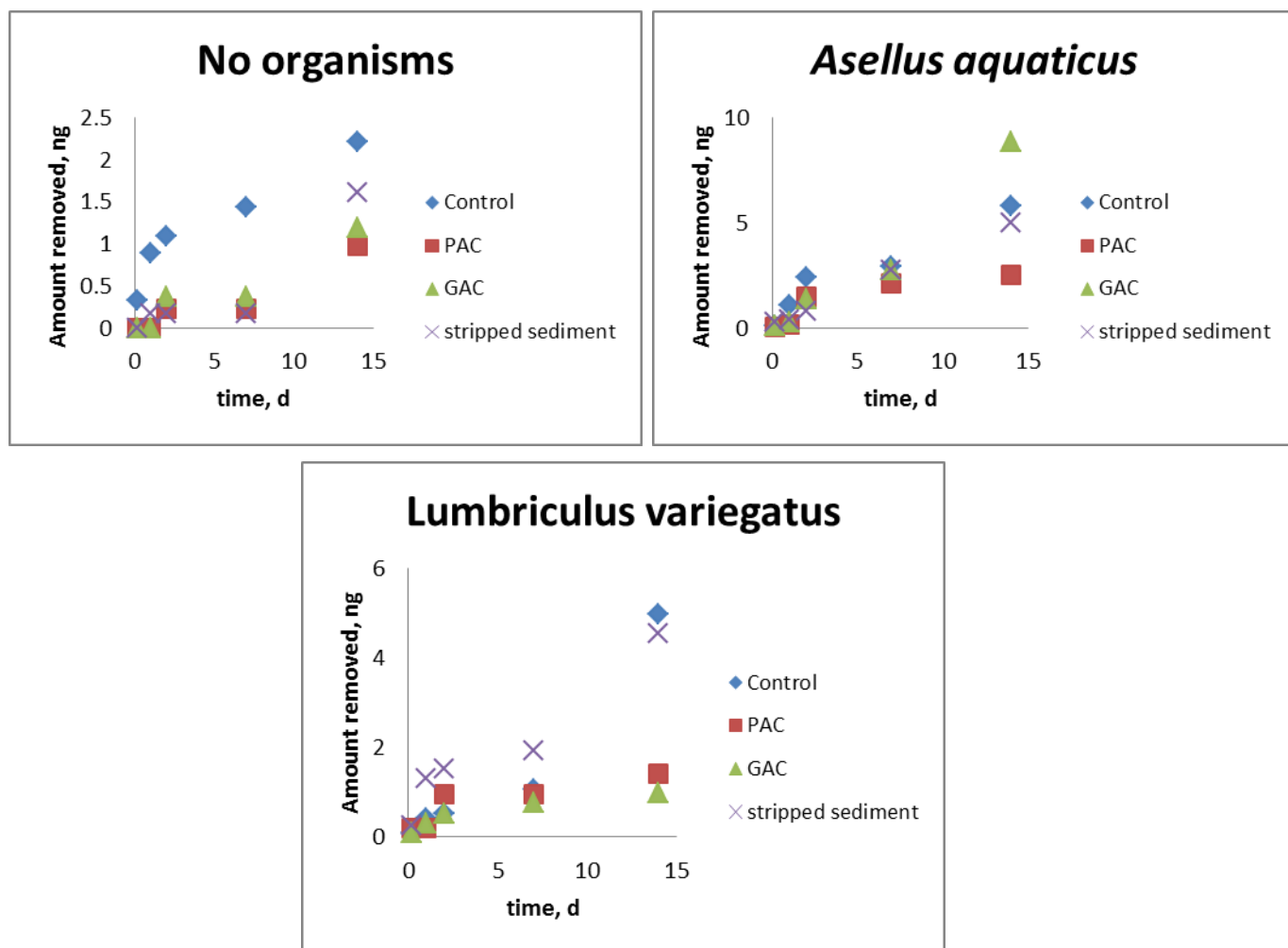
Figure 9 Measured extracted mass of CB-204 from overlying water using Empore disks, for non-bioturbated system (A) and systems with *A. aquaticus* (B) and *L. variegatus* (C) in different AC treatments.

From the obtain results it is evident that irrespective to PCB congener the amount released from the sediment was highest where there is no sorbent material (control) and almost all system PAC was found as most effective sorbent. Release of contaminants increases in presence of bioturbators and *A. aquaticus* had the highest effect since the maximum amount of released PCBs was found with this bioturbators. This fact was also manifested in the turbidity measurement where presence of *A. aquaticus* mostly turbid the systems i.e. most vigorous in bioturburation activity.

It was also seen that the amount of contaminant release reduced as the number of chlorine increased in the PCB congener. Since hydrophobicity of PCB increases with the number of chlorine in its structure which increases the sorption tendency towards the sediment, eventually decreases the desorption pool towards the overlying water. Consequently the contaminant could not release easily from the sediment bed. Hydrophobicity could be expressed by octanol-water coefficient LogK_{ow}. The reported LogK_{ow} values of three representative CB congeners are listed in table 2. The higher the logK_{ow} value, slower the

desorption from the sediment is [22]. CB-204 has the highest LogK_{ow}, thus superior hydrophobicity among the three PCBs; sunsequently, it will more likely be absorbed onto the sediment and diminished the sediment-to-water release. However the presence turbicid increased the release of hydrophobic compounds to the water phase by bioturabation action. Application of AC (both PAC and GAC) reduces the release of PCB to the overlying water, despite the bioturbation activity.

Table: 2. Reported LogK$_{ow}$ values of three representative PCBs

PCBs	IUPAC name	no. of chlorine	Log Kow
CB 52	2,2',5,5'-tetrachlorobiphenyl	4	5.85
CB 138	2,2',4,4',5,5'-hexachlorobiphenyl	6	6.83
CB 204	2,2',3,4,4',5,6,6'-Octachlorobiphenyl	8	7.3

Conclusion:

Since the lowest amount of PCBs released from the PAC treated sediment in almost all system, it is concluded as the most effective treatment. Thus PAC reduces the risk from the contaminated sediment most. The second most effective is stripped treated sediment next GAC treated sediment. The sediment without sorbent material remains its risk where highest mortality was found in case of both organisms.

Presence of bioturbator stimulates the release of the contaminants substantially because of their bioturbation activity and poses higher risk from the contaminated sediment towards the non-benthic organisms. However, in presence of PAC the bioturbators failed to do its bioturbation activity suitably and exhibited less influences on desorption of the contaminants whereas, in presences of GAC and stripped sediment bioturbator able to influence the release of contaminants considerably than PAC treated system. Among the two bioturbators *A. aquauticus* found more sensitive towards PCBs while *L. veriegatus* found sensitive in presences AC.

Moreover, the higher hydrophobic compound adsorbed by the sediment more and lessens the release of bioavailable concentration to the overlying water which ultimately, reduces the risk on the aquatic organisms by the compound .

In conclusion we can state that the desorption pool of POPs increase by the bioturbators but it weakens with the application AC (PAC, GAC and stripped sediment) as well as the desorption pool decreases with increasing hydrophobicity of the respective compound.

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Appendix 1:

1.1 Sediment Pre-treatment for the experimental ditches

Figure 1.1 scheme of the Biesbosch sediment pre-treatment for the
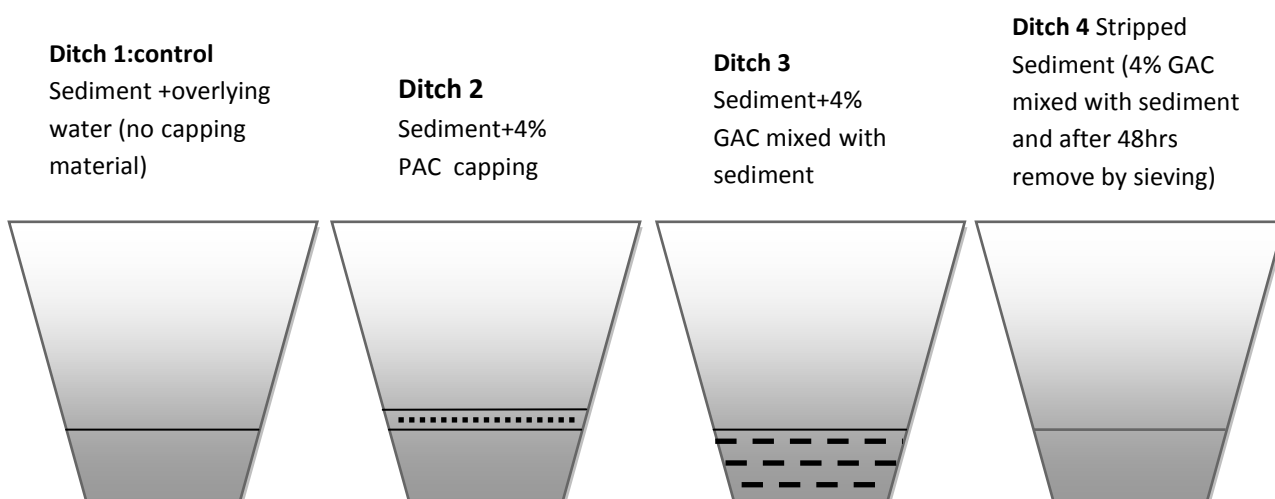
1.2 Treatments Ditches

Ditch 1:control
Sediment +overlying water (no capping material)

Ditch 2
Sediment+4% PAC capping

Ditch 3
Sediment+4% GAC mixed with sediment

Ditch 4 Stripped Sediment (4% GAC mixed with sediment and after 48hrs remove by sieving)

Figure1.2 Scheme of the treatment ditches in the research field Sinderhoeve

Appendix 2

Scheme of the laboratory flux experiment

Cylindrical Core

No capping

4% PAC

4% GAC

Stripped Sediment

C   A   L   C   A   L   C   A   L   C   A   L

▢ → Overlying water
▮ → Sediment
■ → PAC capping
▢ → Empty space
○ → GAC

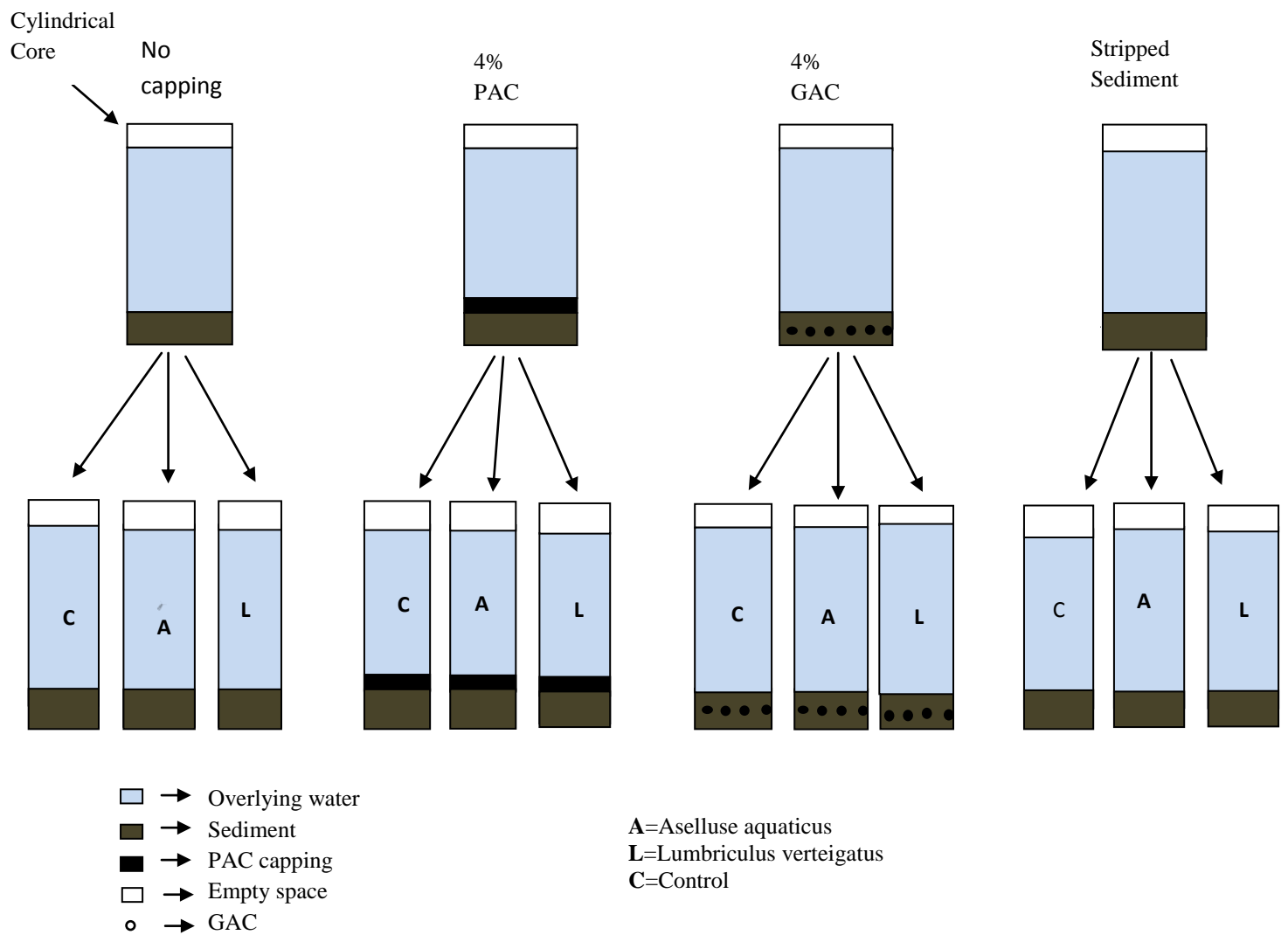**A**=Aselluse aquaticus
L=Lumbriculus verteigatus
C=Control

Figure 2 Scheme of laboratory flux experiment

Figure 3 Measured extracted mass of CB-52 from overlying water using Empore disks, for bioturbated systems in (A) control, (B) PAC, (C) GAC, and (D) stripped sediment.
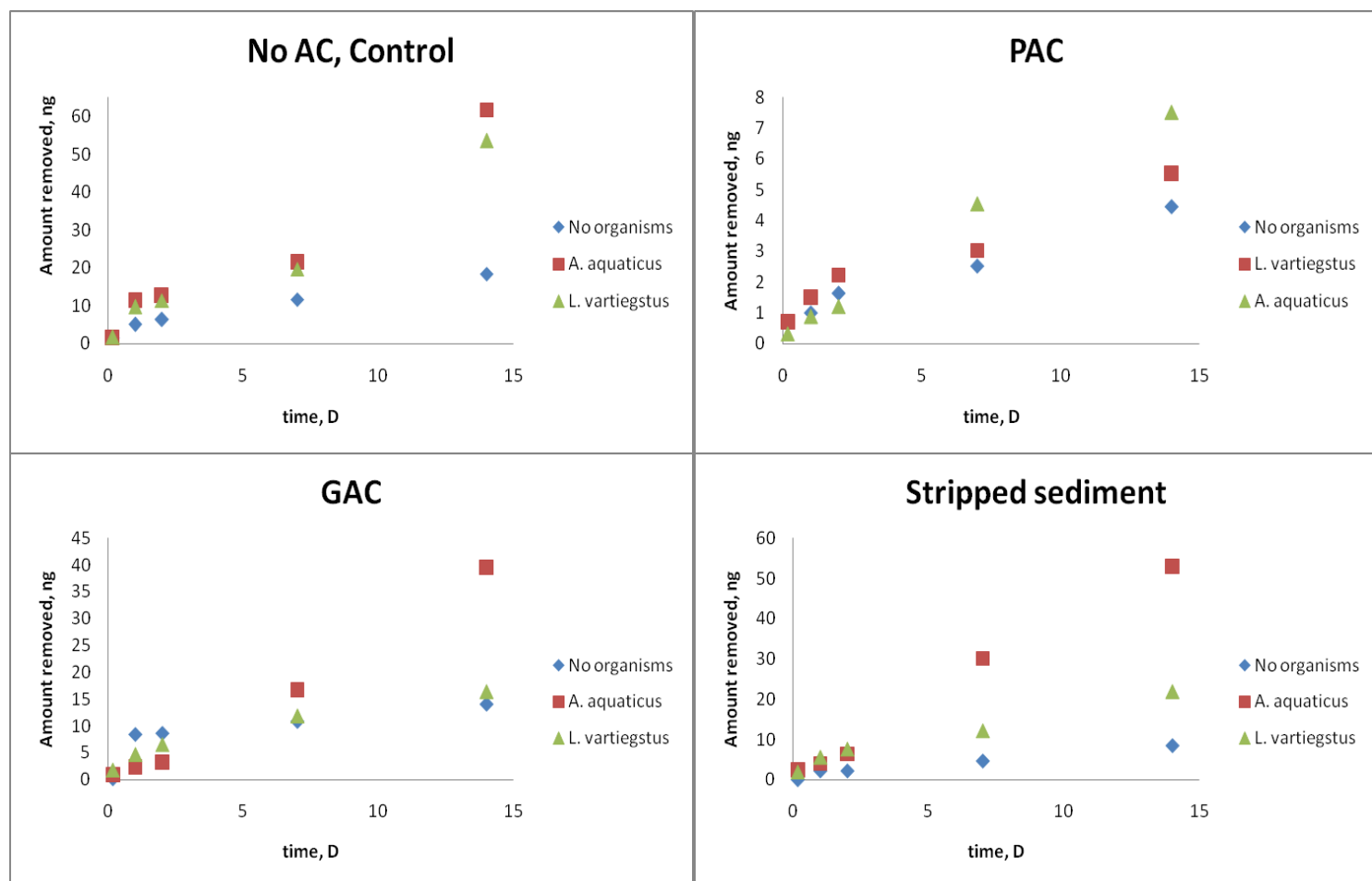
Figure 4 Measured extracted mass of CB-138 from overlying water using Empore disks, for bioturbated systems in (A) control, (B) PAC, (C) GAC, and (D) stripped sediment.
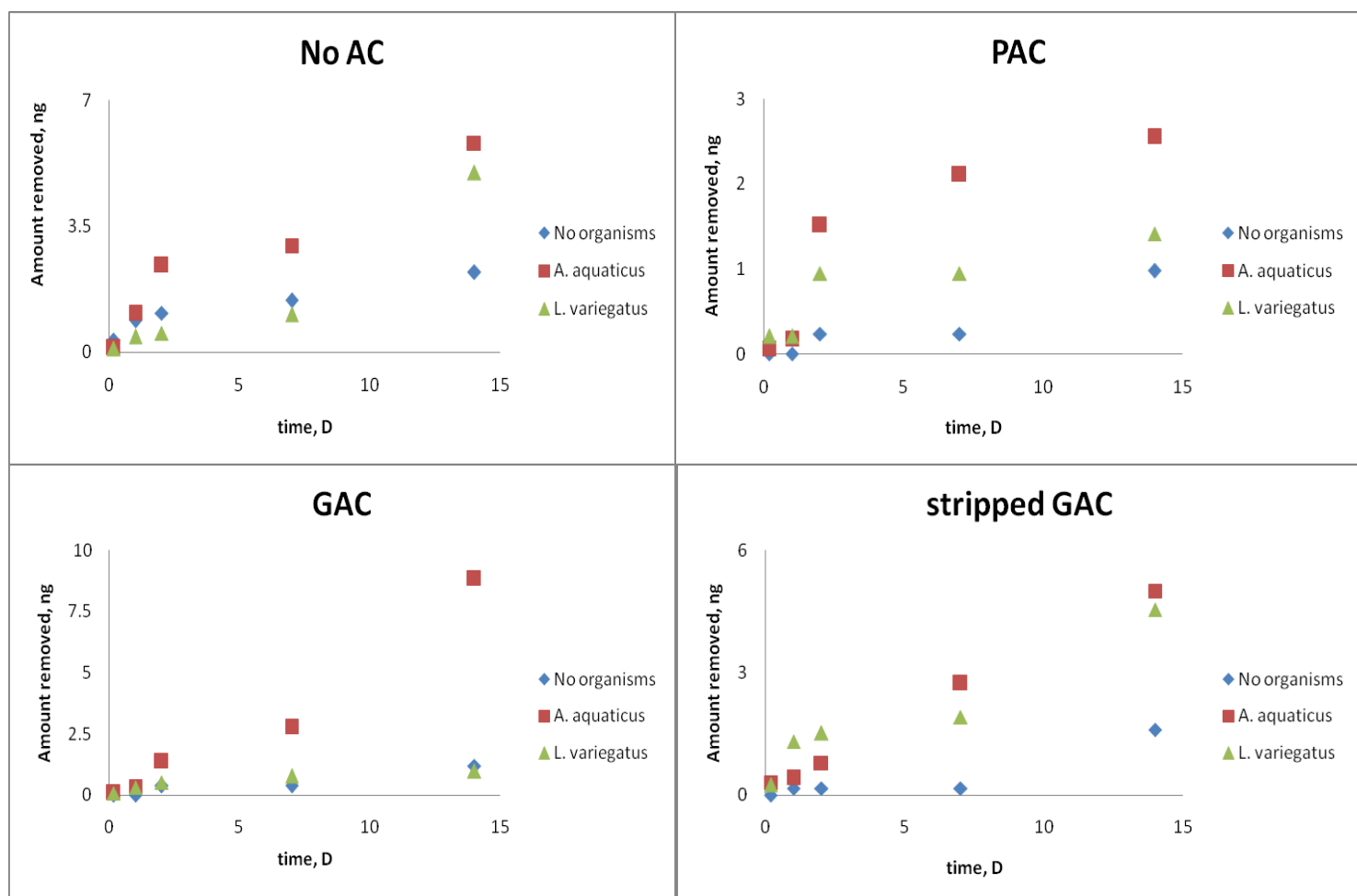
Figure 5 Measured extracted mass of CB-204 from overlying water using Empore disks, for bioturbated systems in (A) control, (B) PAC, (C) GAC, and (D) stripped sediment.