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TNA PROJECT REPORT

1st Call of Proposals
12 January – 3 April, 2012

A) General Information

Proposal reference number(1)	CALL_1_4
Project Acronym (ID) (2)	o-DGTSPOCME
Title of the project(3)	Organic - Diffusive Gradient in Thin-film for sampling polar organic chemicals in marine environment
Host Research Infrastructure(4)	Ferryboxes and Fixed station – Cuxhaven (Germany)
Starting date - End date(5)	11/09 – 03/11, 2013
Name of Principal Investigator(6) **Home Laboratory** **E-mail address** **Telephone**	Kevin C. Jones Lancaster Environment Centre, Lancaster University k.c.jones@lancaster.ac.uk +44 1524 510230
Additional users (7)	Hao Zhang, Prof. in Environmental Chemistry, LEC, Lancaster University, UK, **h.zhang@lancaster.ac.uk**, remotely and Chang'er Chen, PhD student, LEC, Lancaster University, UK, **c.chen3@lancaster.ac.uk**, physically.

B) Project objectives (max. 250 words) (8)

Test the o-DGT samplers for applications in seawater to measure polar organic chemicals like antibiotics;
Deploy the DGT samplers in pilot studies aboard the ferries (collaborated with NIVA) and at the fixed station (collaborated with HZG);
Estimate the water flow rate on the measurement of o-DGT in the flow through sampler and in the estuary;
Compare o-DGT sampler with another passive sampler-ceramic dosimeter (CD);
Investigate the spatial distribution of polar pollutants in the sea between Oslo and Kiel;
Prepare publications and consider a joint bid for further funding embracing wider applications.

C) Main achievements and difficulties encountered (max. 250 words) (9)

Achievements:
1. Found a better deployment solution for ferrybox under the colleagues from NIVA, that is using plastic net to hold the samplers which can separate the samplers but can also deploy batch of samplers together (which is easy for retrieving later);
2. Deployed and retrieved all the samplers deployed in the ferrybox. Six antibiotics were detected in the ferry o-DGT samples but only 4 antibiotics in the CD samples. The results show that o-DGT cannot continuously accumulate antibiotics after 27 days; spatial distribution along this color line cruise was observed for some antibiotics, seems higher levels near the ferry stations (Oslo and Kiel).
3. Successfully deployed the o-DGT samplers in the fixed station (Elbe river estuary) with the DGT holders designed by colleagues from HZG, and retrieved all the o-DGT samplers. Nine antibiotics were

detected in the o-DGT samples, with 3 in the CD samples. Most antibiotics can be continuously accumulated until about 27days. A DBL of 320 um was obtained in this river mouth.

Difficulties encountered:

1. Refill the chambers with pure water after retrieve samplers every time;
2. (bio)fouling for longer deployment time in the ferrybox (> 30 days) and fix station (> 20 days)
3. Lost some CD samplers or the cap opened and the resin come out in the fix station, a better way to protect the dosimeter is needed.

D) Dissemination of the results (10)

We would like to prepare two scientific articles for publication in relevant journals: one for the ferrybox tests (co-author with NIVA colleagues) and another for the fix station deployment in the estuary (co-author with colleagues from HZG). Acknowledgements to EC and JERICO will be included in all the publications; and of course the results will be reported to the JERICO project relevant meeting/workshop later; these results might be also showed to people interested like colleagues from NILU in order to compare or to discuss further opportunities for joint projects.

E) Use of the Infrastructure/Installation (11)

	In situ	By remote
Nr. of Users involved	1	2
Access units (days/months/etc)	days	days
In situ stay day / Remote Access duration	11 days	38 days

F) User project scientific field

Main field (12)	Earth Sciences & Environment
Scientific description (13)	Environment

H) Technical and Scientific preliminary Outcomes (max. 2 pages) (14)

Technically:

1. A better way for deployment of o-DGT samplers in different scenarios was found, which could improve the deployment design of this sampler; 2. Deployment of dosimeter samplers without protection might result in loss of samplers, a better deployment sign is needed; 3. Proper clean procedure is need for cleaning the used CD samples.

Scientifically:

All samples were extracted and analysed by LC-MS/MS for 40 antibiotics according to our previous study (*Chen et al. ES&T, 2013, 47, 13587*). Six antibiotics (LIM, TMP, SPD, CFX, SMX and SDM) were detected in the o-DGT samples and 4 (LIM, SPD, SMX and SDM) in the CD samples from the ferrybox, while 9 antibiotics (LIM, SPD, TMP, SMZ, OFX, CFX, SFX, SMX and SDM) in the o-DGT samples (fig 2) and only 3 (LIM, SPD and SMX) of them in the CD samples from the fix station (Cuxhaven). There were very limited antibiotics detected in the PES filter indicating the suitability of PES as the filer for o-DGT for antibiotics.

In the Cuxhaven, most detected antibiotics can be accumulated continuously in the o-DGT samplers up to 27 days (Fig1.), thus the data from the first 6 days and for the 13 days are suitable for back calculating the concentrations of these antibiotics in the water from Elbe River mouth. o-DGT samplers with different thicknesses of diffusive gels were also deployed for 13 days; these were used

to estimate the DBL which was 320 um. This DBL was then used to calculate the water concentrations of these antibiotics which ranged from 9.3 ng/L (SPD) to 93 ng/L (CFX). The results show that FQs (OFX, CFX and SFX) were the most abundant antibiotics followed by SAs (SMX, SDM, SMZ, SPD) and TMP, LIM. Only LIM SPD and SMX were detected in the CD samplers (which is unexpected), in both deployment times 6 days and 13 days, however, there seem no differences between this two times in terms of the accumulated masses of these antibiotics. Therefore, CD samplers cannot be reused if not being cleaned properly.

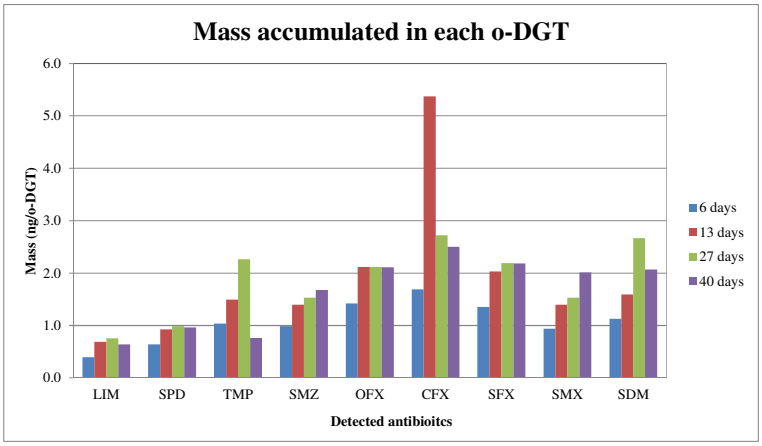

Fig1. Antibiotics detected in the o-DGT samplers deployed for different times in Cuxhaven (fixed station).

On the ferrybox, generally fewer antibiotics and lower levels of them were detected in the samplers from the ferrybox, which is expected because of the dilution effect of the sea. In order to detect more antibiotics, more paralleled o-DGT samplers should be deployed and pool together in the future. Of the 6 detected antibiotics in the o-DGT samplers, LIM was the most frequently found one (up to about 200 pg/o-DGT, only no detection in the samples for 48 days deployment) (Fig2A), followed by SDM (up to about 70 pg/o-DGT), and TMP (only detected in the 38 days' samplers, Fig2B, up to 50 pg/o-DGT), while CFX and SMX were only detected in few samplers with CFX in the 12-day and 27-day samplers in chamber 1 and 12-day samplers in chamber 5 and SMX only in the 12-day samplers in chamber 5. The spatial distribution differences were observed for TMP and SDM: seems a higher level of these antibiotics in the start/end (near Kiel or Oslo) of the journey. While for LIM, there seems no significant difference through these five areas. Again for the CD samplers, the antibiotic components (SMX was the most frequently found one) were different from the ones in the o-DGT samplers. However, the similar spatial distribution trends were observed for LIM and SDM in the CD samplers.

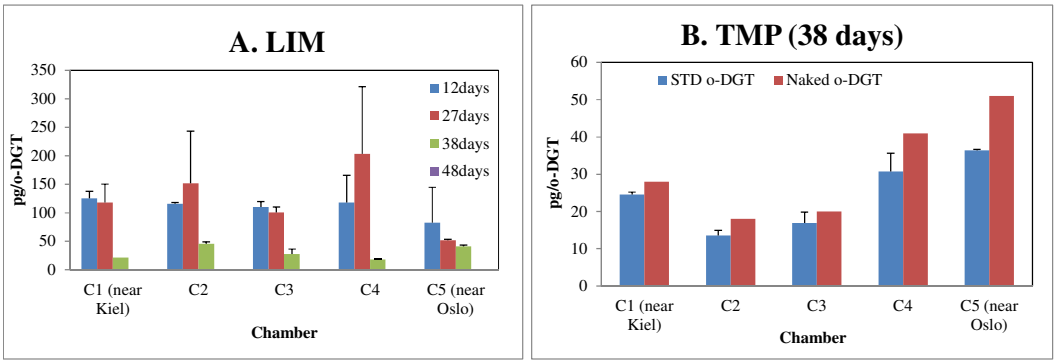

Fig2. LIM in o-DGT samplers for different chambers (areas) at different times on the ferrybox (Oslo - Kiel).