

Impulse Programme Marine Sciences 1992-1996

Project n° 4

**Intercompartment distribution of
monocyclic aromatic hydrocarbons
and C₁-C₂ organochlorines
in the North Sea environment**

**Non-technical
Summary**

Department of Organic Chemistry

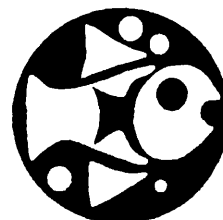
**Faculty of Agricultural & Applied
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University of Gent



Fisheries Research Station

**Centre for Agricultural Research
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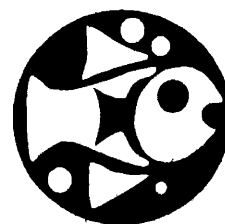
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Research Group:

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REPORT *IMPULSE PROGRAMME MARINE SCIENCES 1992-1996***PROJECT N° 4: NON-TECHNICAL SUMMARY****1. Administrative data of the participating research groups****1.1. University of Ghent**

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Promotor: Prof. Dr. ir. Herman Van Langenhove
Head of the Department: Prof. Dr. Niceas Schamp
Participating researchers: ir. Jo Dewulf: financed by the project from 1/12/92 to 30/10/95. From 1/11/95 participating to the project but not financed by the project.
ir. Benedicte Heireman: financed by the project from 01/01/96.

1.2. Ministry of Agriculture, Centre for Agricultural Research

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Promotor: Dr. P. Hovart (until July 1995)

Dr. ir. W. Vyncke (from July 1995 onward)

Participating researchers

and co-workers:

Patrick Roose: working on the project but not financed by the project

Kris Cooreman: working on the project but not financed by the project

Pascale Driessens: working on the project and financed by the project for the entire period.

Ides Dobbelaere: working on the project but not financed by the project

Marc Van Ryckeghem: working on the project but not financed by the project

Omer Dekock: working on the project but not financed by the project

2. Execution of the project

2.1. Overview of the execution of the project

Table 1 represents the different tasks of the projects as they were in the technical annex of the contract nr. MS/02/42. For each task the responsible research group (column RRG) and a reference to the part of the final report, in which the results for each task are to be found, are indicated.

The tasks:

- A. Preparatory analytical work
- B.1.1. Interspecies, interspecimen variability and sediment samples
- B.1.2. Variability of air and water samples on one sampling location
- C. Study of the air/water exchange; equilibrium partitioning and modelling
- D. Evaluation of sublethal effects.
- E. Evaluation and report

are executed according to the initial planning.

The tasks 2.1. and 2.2. are partially carried out because of two reasons. First, more time was needed in order to start and develop the analytical methods (See point 2.2.). Moreover, the analysis of biota samples took more time than initially planned as a result of the specific difficulties related to this matrix and the long sample processing time. Next, a number of samplings was not executed, because of bad weather conditions or because of the non-availability of campaign time of the research vessel the Belgica.

Additional to the initial programme in each monitoring campaign, an additional location was sampled, i.e. a sampling point which was considered as a reference sampling location, far from the coastline. Secondly an additional number of water samples were taken in the Scheldt estuary in 4 monitoring campaigns in order to improve the understanding of the concentration profiles of the target compounds in the estuary.

2.2. New scientific findings

A. Analytical procedure for the target compounds in air, water, sediment and biota

For the target compounds (i.e. monocyclic aromatic hydrocarbons and C₁- and C₂-chlorinated hydrocarbons) in the air and water compartment, analytical procedures were developed and evaluated. The techniques allowed to analyse the target compounds at the parts per trillion (ppt) concentration level. In a same way appropriate analytical methods were developed for the measurement of the target compounds in biota and sediment.

B. Measurement of the target compounds in the air and water compartment on the Belgian Continental Shelf in the North Sea and in the Scheldt estuary

By the application of the developed analytical methods, from 1993 on 3 to 4 water samplings a year were carried out on 5 locations on the Belgian Continental Shelf and on 2 locations in the Scheldt estuary. Concentrations were in the ppt range, with some obvious higher concentrations of the chlorinated target compounds in the Scheldt estuary. Since 1994 simultaneous air samples were taken. They also showed concentrations of the target compounds in the ppt range.

C. Concentration profile of the target compounds in the water compartment in the Scheldt estuary (trajectory Antwerp-Vlissingen)

In 1995 concentration profiles of the target compounds in the water compartment were established in the Scheldt estuary (Antwerp-Vlissingen). From the obtained profiles it is clear that for a number of chlorinated compounds the water/air exchange is an important transport mechanism. It has to be mentioned that the knowledge on the air/water exchange for the target compounds is rather limited in this type of environment. Additional research in this field can provide a better understanding and a quantification of this transport mechanism.

D. Measurement of the target compounds in the sediment and in biota in the North Sea environment

The results for the measurements of the target compounds in the sediment in the North Sea environment indicate a low, hardly detectable concentration level. Concentrations in biota are in the

same order of magnitude as those of polychlorinated biphenyls and organochlorine pesticides (about 10ng/g). Moreover, the concentrations in biota are on average 30 to 2000 times higher than in the surrounding water. These results are important for the elaboration of a new Joint Monitoring and Assessment Programme of the Paris Commission.

E. Laboratory experiments for the investigation of the air/water equilibrium partitioning of the target compounds

By means of laboratory experiments factors affecting the air/water equilibrium partitioning of the target compounds were investigated. The study allowed to establish a functional relationship between the equilibrium partitioning and the determining factors (temperature and salinity). Further on, the results proved that both the compartments air and water are important environmental compartments in which the target compounds are partitioned.

F. Laboratory experiments for the investigation of the water/sediment equilibrium partitioning of the target compounds

Laboratory studies on the examination of the partitioning of the target compounds between the water column and the sediment showed that the sorption on and the uptake by the sediment of these compounds is rather limited. This can be expected from the physico-chemical properties of the target compounds. From this observation it can be concluded that the role of the sediment as a sink of the target group is rather secondary.

G. Study of the air/water flux of the target compounds in the North Sea environment.

From the determination of the concentrations in air and water and from the study on the air/water equilibrium partitioning, the flux of the target compounds was calculated by means of the available air/water exchange models. For most cases a water to air transfer was noticed, in the range of a few $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. This means that for the Belgian Continental Shelf Sea a mass flux of one single target compound is in the order of 10kg a day.

H. Study on the air/water flux of the target compounds in the Scheldt estuary

From the measurements of the target compounds in air and water in the Scheldt estuary, the water to air transfer of a number of chlorinated compounds proved to be some order of magnitudes higher than for the Belgian Continental Shelf Sea. It is clear that these pollutants brought in the Scheldt are partially removed by a water to air transfer along the trajectory Antwerp-Vlissingen.

2.3. Occurred problems during the execution of the programme

The major problem which occurred during the project was that there was more time needed than provided for the starting and optimization of the analytical methods. Some reasons can be mentioned: the low concentration levels to be measured, the interferences with new matrices examined (especially biota); problems with commercially available sample preparation equipment, which proved to be less performant than it was proposed; sometimes inadequate support of the suppliers of the equipment. The occurred problems were solved and moreover the methodology was constantly subjected to improvement and sufficient quality control in order to obtain reliable measurement data.

The mentioned problems affected the execution of the monitoring campaigns, especially with respect to the large number of samples to be analysed in the original programme. On the other hand, a number of additional analyses were carried out. Systematically a reference location (number 800) was sampled in order to determine the marine background concentration level. Further on, in a number of campaigns water samples were taken on 8 to 10 locations in the Scheldt estuary along the trajectory Antwerp-Vlissingen. Obvious concentration profiles were measured. These data are very useful for the study on the behaviour of the target compounds in the environment.

Table 1. Overview of the execution of the project and reporting

TASKS	RRG	report
A. PREPARATORY ANALYTICAL WORK		
A.2. Starting the GC-MS system at FRS	FRS	II
A.2. Evaluation of analytical procedures		
A.2.1. evaluation air and water analyses	UG	II
A.2.2. evaluation sediment and biota analyses	FRS	II
A.3. Evaluation air sampling systems	UG	II
B. MONITORING of the target compounds in the environmental compartments		
B.1. Variability (specimen en species) within one location		
B.1.1. variability for sediment and biota samples	FRS	III
B.1.2. variability for air and water samples	UG	III
B.2. Monitoring		
B.2.1 analysis of sediment and biota samples	FRS	III III.4
B.2.2 analysis of air and water samples	UG	III III.1 III.2
C. EXCHANGE AIR/WATER, MODELLING		
C.1. Literature study on the behaviour of the target compounds	FRS/UG	I
C.2. Determination of the air/water partitioning coefficients		IV
C.2.1. Monocyclic aromatic hydrocarbons	UG	
C.2.2. Chlorinated compounds	FRS	
C.3. Modelling of the atmosphere/marine environment exchange	UG	IV
D. EVALUATION of possible SUB-LETHAL EFFECTS		
D.1. Starting of the in vitro experiments	FRS	V
D.2. Analysis of the samples of D.1.		
D.2.1. analysis air and water samples	UG	V
D.2.2. analysis sediment and biota samples	FRS	V
E. EVALUATION and REPORTING		
	UG/FRS	

3. Valorisation of the research

3.1. Reports

Final report of the project, consisting of:

Summary

- Part I Literature study
- Part II Evaluation analytical methods
- Part III Monitoring of the target compounds
- Part IV Physico-chemical behaviour of the target compounds and modelling
- Part V In vitro determination of sublethal effects of the target compounds

- Annex III.1 Numerical data on the monitoring results of the target compounds in air
- Annex III.2 Numerical data on the monitoring results of the target compounds in water
- Annex III.4 Numerical data on the monitoring results of the target compounds in sediment and biota
- Annex IV.3 Numerical data on the physicochemical behaviour of the target compounds in the marine environment

3.2. Publications

- J. Dewulf, D. Drijvers, H. Van Langenhove. Measurement of Henry's law constant as function of temperature and salinity for the low temperature range. *Atmospheric Environment* 29(3) 1995, 323-331.
- J. Dewulf and H. van Langenhove. Simultaneous determination of C1- and C2-Halocarbons and monocyclic aromatic hydrocarbons in marine water samples at ng/L concentration levels. *International Journal of Environmental Analytical Chemistry* 61(1995) 35-46.

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- J. Dewulf, D. Ponnet and H. Van Langenhove. Measurement of atmospheric monocyclic aromatic hydrocarbons and chlorinated C1- and C2-hydrocarbons at ng/m³ concentration levels. *International Journal of Environmental Analytical Chemistry*, 62 (1996) 289 - 301.

 - H. Van Langenhove and J. Dewulf, Monitoring 13 priority pollutant VOCs in the North Sea environment. In "Nowe Materiały i Technologie Stosowane w Chemii Środowiska", B. Buszewski Ed., Top Kurier, Torun, Poland.

 - H. Van Langenhove and J. Dewulf. Priority VOCs in the North Sea and the river Scheldt. In proceedings of "The 1st Symposium on Analytical and Environmental Problems", Szeged Hungary September 11-13

 - J. Dewulf, H. Van Langenhove and M. Everaert. Solid Phase Microextraction (SPME) of volatile organic compounds: estimation of the sorption equilibrium from the Kovats index, effect of salinity and humic acids and the study of the kinetics by the development of an "agitated/static layer" model. Accepted for publication in *J. Chromatogr. A* (in press)

 - J. Dewulf, T. Dewettinck, A. De Visscher and H. Van Langenhove. Sorption of chlorinated C1- and C2-hydrocarbons and monocyclic aromatic hydrocarbons on sea sediment. Accepted for publication in *Water Research* (in press)

 - J. Dewulf and H. Van Langenhove. Chlorinated C1- and C2-hydrocarbons and monocyclic aromatic hydrocarbons in marine waters: an overview on fate processes, sampling and analysis, and measurements. Accepted for publication in *Water Research* (as a review)

 - J. Dewulf and H. Van Langenhove. Analytical aspects of the measurement methods and measurement data of 7 chlorinated C1- and C2-hydrocarbons and 6 monocyclic aromatic hydrocarbons in remote air masses: an overview. Submitted for publication in *Atmospheric environment*.

-J. Dewulf, M. Everaert and H. Van Langenhove. Prioritair vluchtige organische stoffen in het Schelde-traject: Gent-Antwerpen-Vlissingen. accepted for publication in the journal Water (in Dutch).

- J. Dewulf and H. Van Langenhove, EPICS determination of Henry's law constant of C₁ and C₂ chlorinated hydrocarbons and monocyclic aromatic hydrocarbons as function of temperature and salinity for the low temperature range, In proceedings of a symposium held on the occasion of the 10th anniversary of the civil service oceanographic research vessel Belgica, Ostend, 17-19 October 1994, 232.

- P. Roose, Chlorinated alkanes in the marine environment. Report of the Advisory Committee on the Marine Environment. Annex 4, ICES, Kopenhagen, Denmark, 1995.

- P. Roose, Benzene and its C₁-C₂ alkyl derivates in the marine environment. Report of the Advisory Committee on the Marine Environment. Annex 5, ICES, Kopenhagen, Denmark, 1995.

-Vyncke, W., Guns, M., Roose, P., Cooreman, K., De Clerck, R. and Van Hoeyweghen, P. Contaminants in Belgian Fish and Shellfish (1971-1993). In: Proceedings of the Symposium "Dialoog tussen de Wetenschappers en de Gebruikers van de Zee." Oostende, 1994.

3.3. Communications

- Participation to JEP Intensive Course VOLATILE ORGANIC COMPOUNDS (VOC) in the Environment, 23-28 augustus 1993, aan U.G., Gent (Tempus programme):

- Prof. dr. ir. H. Van Langenhove: chairman.

- 'Canister sampling and calibration of VOC analysis': contribution by ir. J. Dewulf

- Oral communication on the General Meeting of the Belgian Commission IAWQ (International Association on Water Quality) (22 pp., 38 ref., in Dutch) on 6/5/1993, by ir.

J. Dewulf, title: 'Wisselwerking lucht- en waterpollutie: flux van organische verbindingen tussen water- en luchtmedium'.

- H. Van Langenhove, Monitoring 13 priority pollutant VOCs in the North Sea environment. Oral communication on the symposium "New analytical techniques in the investigation of environmental problems", 3-5 september 1996, Torun, Poland.

- H. Van Langenhove, Priority VOCs in the North Sea and the river Scheldt. Oral communication presented as invited speaker on "The 1st Symposium on Analytical and Environmental Problems", Szeged Hungary September 11-13

- J. Dewulf, Bepaling van gechloreerde C₁- en C₂-koolwaterstoffen en monocyclische aromatische koolwaterstoffen in mariene watermonsters, oral communication on the 3e Vlaams Jongerencongres van de Koninklijke Vlaamse Chemische Vereniging, 10 April 1996

- J. Dewulf and H. Van Langenhove, EPICS determination of Henry's law constant of C₁ and C₂ chlorinated hydrocarbons and monocyclic aromatic hydrocarbons as function of temperature and salinity for the low temperature range, Poster presentations on the symposium held on the occasion of 10 years Belgica, Ostend, 17-19 October 1994

- J. Dewulf and H. Van Langenhove, The closed two-phase system: a method for the calibration of volatile organic compounds in air samples, poster presentation on Jaarvergadering Vereniging Lucht, Utrecht, Nederland, 14 June 1996

- J. Dewulf and H. Van Langenhove, The environmental partitioning behaviour of chlorinated C₁- and C₂-hydrocarbons and monocyclic aromatic hydrocarbons in the marine environment, Poster presentation for the International Symposium Environmental Biotechnology, 21-24 April 1997, Oostende, Belgium

- J. Dewulf and H. Van Langenhove, Air/water equilibrium partitioning and exchange of priority volatile organic compounds in the marine environment, oral communication on the 2nd PhD

symposium Faculty of Agricultural & Applied Biological Sciences, University of Gent, 23 October 1996, Gent

- J. Dewulf and H. Van Langenhove, Concentration gradients of thirteen priority volatile chlorinated and monocyclic aromatic hydrocarbons in the Scheldt estuary, oral communication on the ICES (International Council for the Exploration of the Sea) Annual Science Conference, 27/9-4/10/1996, Reykjavik, Iceland.

- P. Roose, K. Cooreman en W. Vyncke, Determination of volatile organochlorines and monocyclic aromatic hydrocarbons in marine biota from the Belgian Continental Shelf. poster presented at the ICES (International Council for the Exploration of the Sea) Annual Science Conference, Reykjavik (IJsland), 27/9-4/10/1996

- P. Roose, K. Cooreman, W. Vyncke and U. A. Th. Brinkman, Analysis of VOCs in Marine Biota, poster presented at the days of the "Werkgemeenschap Analytische Chemie", Lunteren, 4 en 5 November 1996.

- Vyncke, W., Guns, M., Roose, P., Cooreman, K., De Clerck, R. and Van Hoeyweghen, P. Contaminants in Belgian Fish and Shellfish (1971-1993). oral communication on the Symposium "Dialoog tussen de Wetenschappers en de Gebruikers van de Zee." Oostende, 16 -17 November, 1994.

3.4. New contacts

- National Institute for Coastal and Marine Management, Middelburg, The Netherlands, Dr. G.T.M. van Eck.

Contacts dealing with the study on the behaviour of organic compounds and modelling of the behaviour of these compounds in estuaries

- Free University of Brussels, Dr. C. Lancelot

Contacts dealing with the study on the potential relationship between algal bloom and the production of a number of target compounds.

-Free University of Amsterdam, Prof. Dr. U. A. Th. Brinkman,

Promoter Ph. D. P. Roose

-Institute for Applied Environmental Research, Stockholm, Prof. Dr. B. Jansson,

Collaboration and contacts in relation to the analysis of VOCs in biota.

3.5. Additional contracts

From the application of the air/water exchange models on the measurement data it proved that the air/water transfer of the target compounds is an important exchange mechanism in the environment. This transfer is especially important with respect to turbulent water systems, e.g. streams. In order to obtain a better understanding of this transport mechanism, an application of a credit was made for the National Fund for Scientific Research (N.F.W.O.) and so the following credit was obtained:

Source: N.F.W.O.

Title: Modelling of the air/water exchange kinetics of volatile organic compounds in non-stationary water bodies as a function of the turbulence level

Time: 1 year

Value: 900 000Bfr. (equipment only)

3.6. Thesis works en PhD thesis works

A. PhD student:

Dewulf Jo:

Temporary title: 'Intercompartment distribution of monocyclic aromatic hydrocarbons and C₁- and C₂-chlorinated hydrocarbons in the North Sea environment'

Faculty of Agricultural and Applied Biological Sciences, University of Ghent

Promotor: Prof. Dr. ir. H. Van Langenhove

B. Thesis students:

Drijvers David ^a:

Title: 'Bepaling van sediment-water-lucht partiticoëfficiënten van C₁-C₂ gechloreerde en monocyclische aromatische koolwaterstoffen'; Afstudeerwerk voorgedragen tot het behalen van de graad van bio-ingenieur (1993-1994)

Faculty of Agricultural and Applied Biological Sciences, University of Ghent

Promotor: Prof. Dr. ir. H. Van Langenhove

Logghe Maureen ^a:

Title: 'Bepaling van monocyclische aromatische verbindingen en C₁-C₂ gechloreerde koolwaterstoffen in zeelucht'; Afstudeerwerk voorgedragen tot het behalen van de graad van bio-ingenieur (1993-1994)

Faculty of Agricultural and Applied Biological Sciences, University of Ghent

Promotor: Prof. Dr. ir. H. Van Langenhove

De Visscher Alex ^b:

Title: 'Interkompartimentalisatie van vluchtige verbindingen: de invloed van diffusieprocessen'; Afstudeerwerk voorgedragen tot het behalen van de graad van gediplomeerde in de aanvullende studies Milieuwetenschappen en -Technologieën (1993-1994)

Faculty of Agricultural and Applied Biological Sciences, University of Ghent

Promotor: Prof. Dr. ir. H. Van Langenhove

Dewettinck Tom ^a:

Title: 'Evenwichtsinstelling en transfersnelheid van gechloreerde en van monocyclische aromatische koolwaterstoffen tussen zeewater en zeesediment'; Afstudeerwerk voorgedragen tot het behalen van de graad van bio-ingenieur (1994-1995)

Faculty of Agricultural and Applied Biological Sciences, University of Ghent

Promotor: Prof. Dr. ir. H. Van Langenhove

Ponnet Dirk ^b:

Title: 'Calibratie van adsorptie-thermische desorptie-GC-analyse voor vluchtige organische stoffen in buitenlucht'; Afstudeerwerk voorgedragen tot het behalen van de graad van bio-ingenieur (1994-1995)

Faculty of Agricultural and Applied Biological Sciences, University of Ghent

Promotor: Prof. Dr. ir. H. Van Langenhove

Di Mercantonio Marissa ^b:

Title: 'Vergelijking van verschillende sorbentia voor bemonstering van vluchtige organische stoffen in buitenlucht'; Afstudeerwerk voorgedragen tot het behalen van de graad van bio-ingenieur (1994-1995)

Faculty of Agricultural and Applied Biological Sciences, University of Ghent

Promotor: Prof. Dr. ir. H. Van Langenhove

Everaert Maarten ^a:

Title: 'Monitoring van prioritair vluchtige organische stoffen in het Schelde-estuarium'; Afstudeerwerk voor te dragen tot het behalen van de graad van bio-ingenieur (1995-1996)

Faculty of Agricultural and Applied Biological Sciences, University of Ghent

Promotor: Prof. Dr. ir. H. Van Langenhove

^a Thesis in the field of the Impulse Programme *Marine Sciences*

^b Thesis with aspects related to the Impulse Programme *Marine Sciences*