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► To cite this version:

D. Cianelli, L. Manfra, E. Zambianchi, C. Maggi, A. Cappiello, et al.. Near-field dispersion of Produced Formation Water (PFW) in the Adriatic Sea: an integrated numerical - chemical approach. *Marine Environmental Research*, 2008, 65 (4), pp.325. 10.1016/j.marenvres.2007.12.001 . hal-00501932

HAL Id: hal-00501932

<https://hal.science/hal-00501932>

Submitted on 13 Jul 2010

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Accepted Manuscript

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PII: S0141-1136(08)00002-0
DOI: [10.1016/j.marenvres.2007.12.001](https://doi.org/10.1016/j.marenvres.2007.12.001)
Reference: MERE 3160

To appear in: *Marine Environmental Research*

Received Date: 8 May 2007
Revised Date: 20 December 2007
Accepted Date: 28 December 2007

Please cite this article as: Cianelli, D., Manfra, L., Zambianchi, E., Maggi, C., Cappiello, A., Famiglini, G., Mannozi, M., Cicero, A.M., Near-field dispersion of Produced Formation Water (PFW) in the Adriatic Sea: an integrated numerical - chemical approach, *Marine Environmental Research* (2008), doi: [10.1016/j.marenvres.2007.12.001](https://doi.org/10.1016/j.marenvres.2007.12.001)

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1 **Near-field dispersion of Produced Formation Water (PFW)**
2 **in the Adriatic Sea: an integrated numerical - chemical approach**

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1 **Abstract**

2 Produced formation waters (PFWs), a by-product of both oil and gas extraction, are separated
3 from hydrocarbons onboard oil platforms and then discharged into the sea through submarine
4 outfalls. The dispersion of PFWs into the environment may have a potential impact on marine
5 ecosystems. We reproduce the initial PFW-seawater mixing process by means of the UM3
6 model applied to offshore natural gas platforms currently active in the Northern Adriatic Sea
7 (Mediterranean Sea). Chemical analyses lead to the identification of a chemical tracer
8 (diethylene glycol) which enables us to follow the fate of PFWs into receiving waters. The
9 numerical simulations are realized in different seasonal conditions using both measured
10 oceanographic data and tracer concentrations. The numerical results show the spatial and
11 temporal plume development in different stratification and ambient current conditions. The
12 analytical approach measures concentrations of the diethylene glycol at a maximum sampling
13 distance of 25 m. The results show a good agreement between field observations and model
14 predictions in the near-field area. The integration of numerical results with chemical analyses
15 also provides new insight to plan and optimize PFW monitoring and discharge.

16

17

18 *Keywords:* Produced Formation Waters, Dispersion, Modelling, Chemical tracer analysis,

19 Adriatic Sea, Environmental Monitoring

1 **1. Introduction**

2 A number of offshore natural gas (CH₄) extraction platforms are currently active in the
3 Adriatic Sea (Mediterranean Sea). During production, Produced Formation Water (PFW), a
4 by-product of both oil and gas extraction originated from water naturally present in geological
5 formations (Formation Water) and water injected in the oil field (Process Water) to maintain
6 reservoir pressure (Henderson et al., 1999), is brought to the surface. PFW contains inorganic
7 compounds (i.e. trace metals), volatile aromatic compounds (benzene, toluene, ethylbenzene,
8 xylenes), semivolatile substances (i.e. naphthalene, phenanthrene, dibenzothiophene),
9 phenols, organic acids and additives (Manfra et al., 2007). PFW is separated from the
10 hydrocarbons on the platforms and then discharged into the sea, where potential effects on
11 biota may occur (Neff et al., 2002; Osenberg et al., 1992; Grant and Briggs, 2002; Cicero et
12 al., 2003; Trabucco et al., 2006). This makes the investigation of the physical and chemical
13 characteristics of PFWs extremely important from the environmental standpoint.

14 After discharge, PFWs may be affected by several different processes, such as dispersion
15 into the sea, volatilization towards the atmosphere and settling at the bottom. In particular, the
16 first main process occurring immediately after discharge is the mixing of the PFW plume with
17 the ambient fluid which determines an immediate PFW dilution and the reduction of its
18 concentration in the sea water (e.g. Baumgartner et al., 1994).

19 In the last decade relevant works published on PFW dispersion (e.g., Berry and Wells,
20 2004; Nedwed et al., 2004) showed the importance of using numerical methods to investigate
21 the fate of PFWs discharged in coastal areas. Washburn et al. (1999) demonstrated, by means
22 of a field and modeling study around a diffuser located in California, that a factor controlling
23 the exposure of organisms to PFWs around the discharge location is the depth of the plume in
24 the water column which, in turn, is modulated by seasonal stratification. Realistic calculations
25 of the fate of the PFW components after discharge and different tools for estimation of

1 environmental exposures at various levels of contaminant have also been developed (Sabour
2 and Tyler, 2004; Neff et al., 2006; Durell et al., 2006). Moreover chemical tracer studies have
3 been recognized as an efficient method to accurately describe PFW pathways into the sea as
4 well as to predict concentrations of both drilling mud and produced water in detail (Smith et
5 al., 2004). Applying a combination of oceanographic techniques and chemical assessment
6 methods on the Australian Shallow Water Ecosystem, Burns et al. (1999) suggested that fast
7 rates of dispersion and degradation processes may prevent any long-term contamination in the
8 sandy sediments.

9 The few studies carried out on this topic for the North Adriatic area pointed out that the
10 short term influence of the natural gas platform structures on surrounding sediments is related
11 more to the installation phase than to the subsequent extraction phase (Fabi et al., 2005).
12 Metal (Zn and As) accumulation (Cicero et al., 2003; Manfra et al., 2007) in sediments and
13 mussels (*Mytilus galloprovincialis*), as well as influences on benthic communities (Trabucco
14 et al., 2006), have been observed at locations very close to the platforms. On the other hand
15 no literature is available, to our knowledge, on the identification of PFWs in the
16 Mediterranean Sea by means of chemical tracers and the use of numerical models to
17 investigate the near field dispersion of PWFs in the Adriatic area.

18
19 In this paper we present the results of an integrated numerical-chemical approach
20 developed to investigate the initial mixing of the PFWs discharged from three offshore natural
21 gas platforms located in the Northern Adriatic Sea. Our research is primarily conceived to
22 relate field and laboratory observations with the near field dilution processes through a
23 numerical process study. The present study introduces a multidisciplinary methodology for
24 the estimation of the presently available monitoring protocol efficiency, as well as the
25 potential effects induced on marine systems by PFW discharges in the Adriatic Sea.

1 A typical method to reconstruct the path of the PFW into the sea consists of adding tracer
2 dyes to the effluent before the discharge (Roldão et al., 1998; Carvalho et al., 2002). The
3 restrictive regulations of offshore platforms often make this approach impractical. In the
4 present work, in order to follow the PFW plume within the marine environment and
5 investigate its dispersion, we analyzed the PFWs' chemical composition and identified some
6 possible chemical tracers of these effluents. We assessed the concentrations of the main
7 groups of compounds typical of produced waters originating from natural gas platforms.
8 Metal concentrations were often under detection limits, while the volatile and semivolatile
9 aromatic hydrocarbons have not always been quantifiable. For polycyclic aromatic
10 hydrocarbons, it was difficult to separate the platform and anthropic contributions. On the
11 basis of these analyses, two chemical additives, diethylene glycol and toluene
12 hydrossibutylate, proved to be the most suitable tracers of the PFWs (Manfra, 2006).

13 We here report the data relative to the diethylene glycol (DEG), which provided the best
14 affordable chemical tracer among the investigated substances. DEG is an additive used on
15 offshore gas platforms to prevent the hydrate formation during the gas-water separation
16 process and to inhibit corrosion events (Ballantyne et al., 2005; Ferrari and Giannuzzi, 2005).
17 The estimate of DEG concentrations in both PFW and seawater samples collected at different
18 distances from the platforms led us to select DEG as PFW tracer. This choice also takes into
19 account that the DEG presence in seawater is exclusively attributable to the PFW discharge
20 and that it is miscible in water, thus allowing tracing of the PFW plume (Weyerhaeuser,
21 2005). Moreover it is worth noting that the competent authorities permit the addition of high
22 DEG concentrations (maximum values of 3500 ppm) to PFWs and these may be easily
23 tracked in the seawater.

24 In this work we focus on the entrainment and initial dilution processes that have been
25 reproduced in the regions of our three platforms by means of the UM3 (Three Dimensional

1 Update Merge) numerical model widely and successfully applied (Baumgartner et al., 1994;
2 Frick et al., 2002) by the US Environmental Protection Agency to simulate the near field
3 mixing. The overall study area, the northern Adriatic Sea, is a shelf zone, characterized by
4 depths less than 200 m, where the circulation system shows a relevant seasonal variability
5 (e.g. Artegiani et al., 1997a-b). As previous theoretical and experimental studies demonstrated
6 (Wu et al., 1994; Petrenko et al., 1998), stratification and current variability around the
7 discharge location are critical for the effluent dispersion. Our simulations are realized in
8 different seasonal conditions (summer and winter) using as model input historical current data
9 and density profiles of the receiving water body as well as the actual outfall pipe
10 characteristics. Measured concentrations of the DEG tracer represent another numerical input.

11 Model results are designed to describe the initial dilution phase of the plume and the extent
12 to which water column stratification and ambient currents affect its dynamics. These results
13 are compared with those of the chemical analyses relative to the tracer concentrations
14 observed in the receiving waters.

15 Using oceanographic observations to reproduce the ambient conditions and initial
16 concentrations of the chemical tracer in the PFW, the UM3 model has proven to be able to
17 predict the initial dilution of the PFW from the three investigated platforms in the Adriatic
18 Sea. The integrated approach has allowed us to evaluate the temporal and spatial distribution
19 of the effluent and has provided suggestions to plan and optimize the PFW discharge
20 protocols as well as the monitoring strategy.

21

22 **2. Materials and methods**

23 *2.1. Field data*

24 In this work we consider three platforms located in the northwestern Adriatic Sea (Fig. 1)
25 As mentioned above, this portion of the basin is characterized by a very wide and shallow

1 continental shelf, and the overall main current in the area is represented by the Western
2 Adriatic Current (WAC), a southeastward coastal current flowing along the Italian coast
3 (Falco et al., 2000)

4 The water column depth at the platforms ranges between 18 and 120 m (Table I); the
5 PFWs are discharged from a single port outfall pipe oriented downward at the depths from 3
6 m above the sea surface to 12 m depth (Table 1).

7 The data utilized in this study come from two monitoring surveys carried out in the
8 summer of 2005 and 2006 (Manfra, 2006): the PFWs were sampled on all three gas platforms
9 (1, 2 and 3 hereinafter) and marine surface water samples were collected during PFW
10 discharge in six stations at increasing distance from the discharge source (0 m - close to the
11 platform – 5 m, 10 m, 15 m, 20 m and 25 m) after a qualitative estimate of the ambient
12 current direction. In the case of platforms 2 and 3, at the farthest station (25 m) subsurface
13 samples were also collected at discrete depths (0 m, 4 m, 8 m, 12 m; at platform 3 also 16 m)
14 in the water column. The samples were stored in dark glass bottles to inhibit photochemical
15 activity and saturated with mercury chloride to inhibit bacterial activity, then were refrigerated
16 at 4°C.

17 A characterization of the dynamic environment in which the PFWs are discharged was also
18 carried out; hydrological data were collected on a number of oceanographic cruises carried
19 out during spring and summer seasons starting in April 2001 through August 2003 (ICRAM,
20 2002, 2003 and 2004). Temperature and conductivity were measured by an Idronaut Ocean
21 Seven 316 CTD sonde at a distance of 50 m from the platform. Hydrographic data for the
22 winter season have been drawn from the Dartmouth Adriatic Data Base
23 (<http://thayer.dartmouth.edu/other/adriatic/databanks/hydrography/hydrography.html>) in the
24 form of seasonal average stratification at the platform locations.

25 Surface currents have been derived from historical surface Lagrangian drifter

1 measurements in the Adriatic Sea from 1994 to 1996 (Falco et al., 2000) (Fig 1). They
2 indicate current values in a range from a minimum of 3 cm s^{-1} to a maximum of 18 cm s^{-1}
3 (Table I) with a southeastward prevailing direction in the area of the platforms, corresponding
4 to the above mentioned WAC. These data were complemented with ADCP data collected
5 between May 1995 and February 1996 (Ursella and Gačić, 2001). Current speeds were
6 considered as uniform with depth down to two meters above the bottom (a typical order of
7 magnitude for the logarithmic bottom boundary layer thickness in both shelf and deep ocean;
8 see Nakata, 1981; Gust and Weatherly, 1985), where the profile assumed a logarithmic shape
9 and a no slip condition was applied.

10 Figure 1 approximate location

11 Table I approximate location

12

13 2.2. Chemical analyses

14 For DEG analysis, the samples were preconcentrated by an off-line solid phase extraction
15 technique (SPE), which provides a concentration factor of about 500 and avoids problems
16 connected to the different salinity of the samples (Cappiello et al., 2007). Each sample was
17 introduced into a cartridge packed with 200 mg of ISOLUTE ENV+, an adsorbent material
18 suitable for polar compounds (International Sorbent Technology, Glamorgan, UK). The
19 cartridge was conditioned beforehand with 15 ml of acetone and then with 10 ml of deionized
20 water. 100 ml of each sample was forced through the cartridges at a flow rate of 5 ml min^{-1} .
21 DEG was eluted with 8 ml of acetone. The extract was evaporated to a volume of $200 \mu\text{l}$
22 under a gentle stream of nitrogen and $200 \mu\text{l}$ of deionized water were then added; finally, after
23 a complete evaporation of the acetone, DEG remained dissolved in $200 \mu\text{l}$ of water.

24 The extract was introduced into the mass spectrometer (Hewlett-Packard 5989A) using a
25 Direct-EI, LC-MS interface in Flow Injection Analysis (FIA) mode (Cappiello et al., 2002).
26 The Direct-EI interface shows several advantages in this specific application: high specificity,

1 very low influence of the mobile phase and matrix composition (Choi et al., 2001; Reemtsma,
2 2001). In particular, residues of salts in the extracts do not affect mass spectral response.
3 Identification of DEG was obtained in Selected Ion Monitoring analysis (SIM) using three
4 characteristic ions (m/z 45, 75 and 76). M/z 75 signal was used in quantitation experiments.

5 The limit of detection (LOD) of the method, expressed as the minimum concentration of
6 the DEG that can be detected in the sample, was $31 \mu\text{g l}^{-1}$. The percentage of recovery for this
7 method was $65.0 \pm 16.3 \%$ (Cappiello et al., 2007) but further studies are currently in progress
8 in order to improve the sensitivity of method.

9

10 2.3. UM3 model

11 The near field dilution is the initial mixing process of an effluent discharged into the sea,
12 due to the combined effects of momentum and buoyancy and acting close to the effluent
13 diffuser (Baumgartner et al., 1994).

14 In the present work the dispersion of a PFW plume in the near field has been simulated by
15 means of the UM3 (Three-dimensional Updated Merge) model specifically conceived for
16 single and multi-port submerged discharges (Baumgartner et al., 1994; Frick et al., 2002) and
17 included in the EPA interface PLUMES (<http://www.epa.gov/ceampubl/swater/vplume>).
18 Compared with other models for the near field mixing, UM3 provides a good prediction of the
19 initial dilution processes for both waste-water (Carvalho et al., 2002) and PFWs discharges
20 (Roberts and Tian, 2004); moreover, strictly dealing with produced water discharges, UM3
21 has proven to accurately reproduce the observed dilutions (Roberts and Tian, 2004).

22 UM3 is a three-dimensional Lagrangian model that quantifies entrainment, the process by
23 which ambient fluid is incorporated into a plume, by applying both the Taylor entrainment (or
24 shear) and the projected-area-entrainment (PAE) (or forced) hypotheses (e.g. Winiarski and
25 Frick, 1976). The equations for conservation of mass, momentum and energy are computed at

1 each time step along the plume trajectory.

2 The dilution process may be considered the outcome of entrainment; it may be enhanced or
3 inhibited by outfall pipe, ambient fluid and effluent properties (Baumgartner et al., 1994)
4 which the UM3 model takes into account as model inputs. In particular, the model considers
5 the diameter and the orientation of the port as well as the depth of discharge as the outfall pipe
6 features which may affect the effluent velocity and the plume trajectory.

7 The receiving ambient fluid properties are described by means of vertical profiles of
8 density, which is the main variable affecting plume buoyancy. The effluent and the ambient
9 density typically differ and the entrainment process tends to cancel this difference; when an
10 equilibrium condition is reached (s.c. *neutral buoyancy level*, or *trap level*) the initial mixing
11 process terminates. The current velocity and direction close to the point of discharge are also
12 important features affecting plume dynamics. The former parameter may increase the shear
13 between plume and ambient fluid thus contributing to the production of turbulence that
14 directly influences the dilution; the second mainly acts on the plume trajectory (Frick et al.,
15 2002). The current profile used in our computations was obtained as described above, in the
16 section on “Field data”.

17 The UM3 model provides output parameters useful to evaluate the space and time
18 evolution of the effluent. The PFW dilution is parameterized through the mass dilution factor
19 (S_a), which is the ratio between the effluent concentration and the cross sectional average
20 concentration in the plume. For a round shaped outfall, the densimetric Froude number
21 (Brandsma et al., 1992), which provides an estimate of the relative importance of momentum
22 and buoyancy in driving the initial mixing, is defined as:

23

24

25

26

27

$$Fr = \frac{U_0}{\sqrt{gD \frac{\rho_a - \rho_e}{\rho_e}}} \quad 1)$$

1
2

3 where D is the outfall pipe port diameter, ρ_a the ambient density at depth of the port, ρ_e the
4 effluent density and g is gravity. U_0 represents the effluent outflow velocity and is given by:

5

$$6 \quad U_0 = \frac{4q}{\pi \cdot D^2} \quad 2)$$

7
8
9

10 with q is the volume flux at outfall pipe port.

11 In order to characterize the stability of the water column at discharge depth we
12 approximate, for each platform, the classic formulation of the Brunt-Väisälä frequency N

13

$$14 \quad N = \left[-\frac{g}{\rho_{ref}} \frac{\partial \rho}{\partial z} \right]^{\frac{1}{2}} \quad 3)$$

15
16

17

18 as in Washburn et al. (1998):

19

$$20 \quad N = \left[-\frac{g}{\rho_{ref}} \frac{\Delta \rho}{\Delta z} \right]^{\frac{1}{2}} \quad 4)$$

21

22

23 where ρ_{ref} represents the ambient fluid density at the depth of the discharge and $\frac{\Delta \rho}{\Delta z}$ is the

24 vertical density gradient in correspondence of the outfall depth. N is computed by finite

25 differencing the measured density profile in a vertical range of 4 m centred around the depth

26 of discharge.

27

28 3. Results and discussion

29 The numerical and chemical results on PFWs discharged by three gas platforms are here

1 discussed. In this work, the PFW characteristics from the offshore gas platforms have been
2 used to run three numerical simulations in summer conditions (see Table II); in this case, as
3 input data we considered the tracer concentration (DEG) measured in sea water (platform 1)
4 and in the effluent (platform 2 and 3). The field current and water mass circulation of the
5 Northern Adriatic Sea present a marked seasonal variability (e.g. Artegiani et al., 1997a-b)
6 which may affect the PFW dispersion. To evaluate the role of stratification on the plume
7 dynamics we also simulate a winter PFW discharge from the three platforms (see Table II)
8 using the same effluent characteristics as in the summer case (average flow, temperature and
9 salinity) and the total PFW concentration. We also compare the vertical DEG profile
10 measured at 25 m from the source with the dilution and path of the plume predicted by the
11 near field model.

12 The chemical results are presented in Figure 2 and Figure 4, while the output data of the
13 UM3 model are summarized in Table II and Figures 3 – 5.

14 Figure 2 approximate location, Table II approximate location

15

16 *Platform 1*

17 The average effluent flow is approximately 27400 l d^{-1} ; the PFW outfall pipe is located 3 m
18 above the surface so that, immediately after the discharge, the PFW sinks into the water
19 column. In the proximity of the platform, the surface DEG content was nearly one third of the
20 initial value (Fig. 2); a surface concentration decrease is observed at 5 m from the discharge
21 point, after which surface DEG values display an increasing trend until the farthest
22 measurement station.

23 The UM3 model simulates the plume trajectory only from outfalls located below the sea
24 surface; here we consider that the plume starts to spread at 2 m depth below the surface, after
25 the initial sinking of the discharged PFW and the effect of air entrainment owing to the impact
26 with the water surface. The initial DEG value used here as input concentration to the UM3

1 refers to the surface concentration detected at 5 m from the source.

2 The measured hydrological structure of the water column in the summer shows a
3 pycnocline (Fig. 3a) at ~12 m, whereas the surface layer, influenced by the PFW discharge,
4 appears homogeneously mixed. A first sinking phase of the effluent induces the low DEG
5 concentrations detected at the surface, close to the PFW source. On the other hand, effluent
6 and ambient water show different densities (23.95 and 25.75 σ_t respectively) which explain
7 the resurfacing of the plume at ~14 m from the PFW source (Fig. 3b) and the consequent
8 increase in the surface measured concentration at 15, 20 and 25 m.

9 In spite of the high effluent flow (Table I), the mixing condition of the surface layer, along
10 with the swift currents associated with the platform location (17 cm s⁻¹), determine a rapid
11 initial dilution ($S_a = 175$ after 1.5 mins) of the DEG tracer.

12 At the simulated discharge depth (2 m) the summer and winter Brunt-Vaisala frequency
13 values are comparable (Table II), even though winter intense mixing leads to a fully
14 homogeneous density profile (Fig. 3a). In the winter season the increased density difference
15 between effluent and ambient water (Table 2) affects plume dynamics both decreasing the
16 extent of initial mixing zone (Fig. 3b) and quickening the initial dilution process ($S_a = 170$ in
17 60 s).

18 Figure 3 a-b approximate location

19 Figure 4 approximate location

20

21 *Platform 2*

22 The PFW showed high initial DEG concentration (9600 $\mu\text{g l}^{-1}$) whereas values about four-
23 five times lower than the initial concentration were recorded in ambient water samples. The
24 outfall is located at 9 m depth and the discharged volume is relatively small (about 11000 l d⁻¹);
25 at 25 m from the source, the DEG surface value is lower than that recorded at 8 m depth
26 (2460 $\mu\text{g l}^{-1}$; Fig. 4).

1 Under summer stratification (Fig. 5a) and low ambient current conditions (the measured
2 surface value is 3 cm s^{-1}), a negative buoyancy is far more relevant ($Fr = 0.66$). As reported in
3 Table II, the PFW is characterized by a density greater than the receiving water at the port
4 depth, which causes an initial sinking in the water column down to $\sim 10 \text{ m}$ depth (Fig. 5b). At
5 the end of the initial mixing phase the plume, not much diluted ($S_a = 55$), remains close to the
6 source point and approximately at the depth where the highest concentrations of DEG have
7 been observed (Fig. 4 and 5b). The comparison between field and model data suggests that
8 the plume is trapped into a narrow layer centered at the discharge depth; the initial dilution
9 terminates very rapidly, developing within only 2.5 m from the source in slightly more than
10 one minute. After the near field dilution, vertical diffusivity processes may affect the plume
11 path determining the maximum DEG concentration observed at 8 m depth; however it is
12 worth to underline that discretised sampling strategy does not allow to reconstruct the vertical
13 DEG profile in detail.

14 A completely different situation is found in simulating the water column winter mixing,
15 when a low stability condition ($N = 0.15$) occurs at the discharge depth. The PFW plume is
16 lighter than the receiving water, shows a Froude number (0.06) with positive buoyancy and
17 rises to $\sim 8 \text{ m}$ depth (Fig. 5b). Current conditions being equal, the intense winter mixing
18 determines a significant increase of the initial dilution extent and time (Table II).

19 Figure 5 a-b approximate location

20

21 *Platform 3*

22 High DEG concentration ($13000 \mu\text{g l}^{-1}$) was measured in the discharged fluid, while in
23 seawater surface samples values about one order of magnitude lower than the initial
24 concentration were detected (Fig. 2). The DEG vertical profile (Fig. 4), similarly to platform
25 2, displays the maximum value ($2810 \mu\text{g l}^{-1}$) at 8 m sampling depth along the water column

1 even though the PFW source is located at 12 m depth and the volume of discharged effluent is
2 low (about 8200 l d⁻¹).

3 During summer, the ambient conditions of platform 3 discharge are similar to those of
4 platform 2 in terms of low current (4 cm s⁻¹) and water column stability ($N = 0.33$) (see also
5 Fig. 6a.). A positive buoyancy ($Fr = 0.15$) leads the plume to slightly rise to ~11.5 m, where
6 the trap level is reached (Fig. 6b). At the end of the initial mixing phase the dilution has
7 reached the value of 74 at ~15 m horizontal distance from the source. In this case the initial
8 dilution process ends in approximately 7 minutes. The model results indicate an initial plume
9 rising in the near field region, after which additional dilution may occur reducing the PFW
10 density and sustaining its further rising in the water column, in agreement with the 8 m
11 maximum DEG concentration measured at 25 m distance.

12 Modifying the water column stratification (Fig. 6a) yields an increase in the density
13 difference between effluent and receiving water (σ_t are 24.8 and 26.5 respectively). The
14 plume shows positive buoyancy and immediately after the discharge starts to rise in the water
15 column reaching the trap level at ~ 11 m depth (Fig. 5b). The low stability of the water
16 column acts to drastically decrease the time dilution and to enhance S_a . It is worth noting that
17 the initial mixing zone extension around the discharge point is less than 7 m.

18 Figure 6a-b approximate location

19
20 Even with the limitations due to the unavailable vertical discretization when it comes from
21 water sampling, the comparison between chemical analyses and numerical simulations
22 showed a good agreement, pointing out the presence of a limited layer within which the
23 plume spreads and evolves. In particular, both outcomes indicate that the plume mainly
24 develops within a layer 2 to 4 meters thick, centered at the discharge depth. Moreover, as in
25 previous experimental studies carried out in similar conditions (e.g. Robert and Tian, 2004),
26 the platforms discharging in the water column in low current conditions are characterized by a

1 near field dilution occurring within 15 m or less from the outfall. It is worth underlining that
2 the UM3 model only simulates the initial dilution phase of the plume, whereas the PFW can
3 also be found in the sea at distances further from the source, where far field processes play a
4 significant role; this is the case here, as shown by the chemical analyses.

5 Since DEG is exclusively attributable to PFW discharge, it is miscible in seawater, is easily
6 measured and can be added to PFW in concentrations as high as 3500 mg l^{-1} , it provides a
7 very convenient chemical tracer of PFWs originating from gas platforms. However, the
8 results have shown that the DEG traceability varies according to the discharge position and
9 the PFW density.

10 All effluent features being the same, the plume dynamics within the water column appears
11 strongly modulated by the seasonal stratification for all modelled current speeds. During
12 summer, the N frequency values are typically greater than in winter, thus indicating a high
13 level of stability at discharge depth. The periods of high stratification also influence the trap
14 level depth of the plume (see Platforms 2 and 3) which is deeper in the summer. In winter
15 conditions, when intense mixing fosters the rise of the plume in the water column, an opposite
16 situation occurs for all the investigated platforms.

17 As suggested by previous studies (e.g Frick et al., 2002), for horizontal outfalls densimetric
18 Froude numbers less than 1.0 typically indicate a fluid so buoyant to rise to the top of the
19 discharge port; in this case ambient fluid may flow into the outfall under the plume. Recent
20 technologies (involving the adoption of special valves) have been developed to prevent this
21 problem by increasing the Froude number via a reduction of the port cross-sectional area in
22 low flow situations (e.g Frick et al., 2002). In this work we only treat platforms with vertical
23 outfall pipes operating in weak current conditions, for which Froude number values less than
24 1.0 indicate that the plumes are dominated by the buoyancy effect (Frick et al., 2004). In our
25 numerical experiments, Fr values less than 1 in both unstratified and stratified scenarios also

1 point out that stratification conditions have a more relevant effect in controlling the plume
2 dilution compared to the current field.

3 Another consequence of the variability in stratification is that the near-field dilution
4 parameter S_a may be highly variable. When the water column is highly stable in summer, the
5 plume is mixed over a smaller region of the water column (Table II), resulting in lower values
6 of S_a . For periods of weaker stratification in winter, the plume mixes over a larger zone of the
7 water column and S_a increases. A particular situation occurs when the discharge mainly
8 develops in the surface mixed layer (Platform 1). In this case the effect of the high currents
9 (17 cm s^{-1}) is clearly predominant with respect to the water column stability, the winter
10 mixing only affecting the time required for the initial dilution and the plume horizontal extent.

11 The initial dilution times resulting from our integrated study are also consistent with
12 observed toxicological data (ICRAM, 2006; Manfra, 2006) revealing low or null toxic effects
13 in the water column close to the Adriatic platforms (stations sampled close to the source and
14 at 25 m, 50 m and 500 m distances). The time required to complete the initial dilution
15 (between 60 and 400 s) allows even the organisms entrained in the plume to be exposed to
16 rapidly decreasing concentrations of pollutants.

17

18 **4. Conclusions**

19 An integrated numerical-chemical approach has been used to investigate the near-field
20 dispersion of the produced formation waters discharged from three offshore natural gas
21 platforms operating in the northern Adriatic Sea.

22 The chemical approach is an analytical procedure which gives accurate concentrations of
23 the single compounds present in PFWs. The observed quantities of a selected contaminant
24 (DEG) have been integrated in the UM3 model allowing a comprehensive description of the
25 initial dilution path and time scales of the PFWs. In addition, measurements of currents and

1 ambient density stratification have been used, representing another model input necessary to
2 assess the role of the physical constraints on the effluent dynamics.

3 All the simulations have been performed neglecting the loss of material contained in the
4 PFWs through removal or degradation processes and assuming a current field uniform with
5 depth, therefore our results may be considered a worst case of PFWs discharge. A good
6 agreement between field chemical data and modelling prediction is obtained even though the
7 comparison is only restricted to the near-field process. Future efforts will investigate times
8 and spatial scales of the far field region.

9 Results show that the plume behaviour is highly influenced by the thermal stratification
10 observed during the summer season, while no effect of the detected DEG concentrations on
11 the effluent density is clearly visible. In the case of submerged discharges, under stratified
12 conditions, the plume appears mainly trapped around the outfall pipe depth and the dilution
13 parameter S_a is relatively low (less than 80), while the presence of weak currents exerts little
14 influence on it. In unstratified conditions the effluent rises in the water column and the
15 dilution significantly increases to more than 130. In agreement with several dispersion/fate
16 models of produced water (Neff, 2002; Nedwed et al., 2004; Berry and Wells, 2004; Smith et
17 al., 2004; Durell et al., 2006) also in our cases the initial dilution processes are very rapid, the
18 fast PFWs dispersion times (< 7 min) causing negligible or no-toxic effects on the marine
19 organisms (ICRAM, 2006; Manfra et al., 2007).

20 In recent years the importance of assessing the influence of the PFWs discharge on the
21 marine environment has been recognized, and monitoring programmes have been successfully
22 developed (Maggi et al., 2007). Our integrated numerical-chemical approach may represent a
23 suitable tool providing advice to optimize both the monitoring activities and the industry
24 discharge practices.

25 For example, the present work clearly shows that under strong stratification conditions the

1 effluent mainly develops its path around the discharge depth. Our results suggest that an
2 improvement of monitoring programmes is needed, for example to plan more samplings along
3 the water column starting close to the platform and up to 1 km from the source. Since the
4 water column stability has a relevant role on plume dynamics, it could also be useful to
5 schedule field measurements during the winter season.

6 Another relevant result achieved in the present work is that the highest effluent
7 concentrations, within the near-field zone, are found with strong stratification and low current
8 speed. Discharging higher volumes of effluent during the winter period could be a good
9 practice, as it would promote the dilution in the near-field.

10 Such indications may be essential to support decision makers in their efforts to mitigate the
11 impacts of the offshore platform operations on the marine ecosystems. Integrated chemical-
12 numerical approaches could also be employed by the regulatory authorities (Frick et al., 2000)
13 - as usually done, e.g. by the US Environmental Protection Agency - to establish the extent of
14 the initial dilution zone (ZID). Even though many definitions exist (Roberts, 1996; Jirka et al.,
15 2004), the ZID may be typically considered as a mixing zone around the discharge point
16 where ambient concentrations may exceed surface water quality standards but acutely toxic
17 conditions must be prevented. The initial dilution zone may be established by the authorities,
18 for example to protect local marine resources (Larsen, 2000); an integrated approach can be
19 used to assess the seasonal extent of the mixing zone, by taking into account the effluent flow,
20 the local current field and the concentration acceptable for the key organisms.

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1 **Acknowledgements**

2 The authors acknowledge comments by the three anonymous Reviewers and F.Bignami. This
3 research has been carried out as the result of a reciprocal agreement between the University of
4 Naples Parthenope and the Central Institute for Applied Marine Research (ICRAM). This
5 work was partly funded by the QUAMACO Project (Plan of activity of knowledge of coastal
6 marine environment) and by the EU Interreg III B Archimed CORI (Prevention and
7 Management of Sea Originated Risk to the Coastal Zone) project.

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1 **Figure captions**

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3 Figure 1 – Adriatic Sea: surface velocity fields as deduced by Lagrangian Drifters (adapted
4 from Falco et al., 2000) and platform positions.

5 Figure 2 – DEG concentrations observed at the sea surface at increasing distances from the
6 three platforms.

7 Figure 3 – a. Summer and winter density profiles close to Platform 1. b. Plume vertical
8 section vs. horizontal distance from the discharge location in summer and winter conditions.
9 The path of the plume is described by means of its centerline (cIn) and boundaries (bnd).

10 Figure 4 - Profiles of DEG concentrations detected along the water column at 25 m from
11 Platforms 2 and 3.

12 Figure 5 – a. Summer and winter density profiles close to Platform 2. b. Plume vertical
13 section vs horizontal distance from discharge location in summer and winter conditions. The
14 path of the plume is described by means of its centerline (cIn) and boundaries (bnd).

15 Figure 6 – a. Summer and winter density profiles close to Platform 3. b. Plume vertical
16 section vs. horizontal distance from discharge location in summer and winter conditions. The
17 path of the plume is described by means of its centerline (cIn) and boundaries (bnd).

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Table I
Field data and input model values

Platform	Distance from the coast	Average effluent flow	Port diameter	Water column depth	Diffuser Depth	Sampling distances from diffuser	Sampling depths	Surface current speed	Effluent salinity	Effluent temperature	Initial DEG conc.
	(Km)	(l d ⁻¹)	(m)	(m)	(m)	(m)	(m)	(cm s ⁻¹)	(g kg ⁻¹)	(°C)	(µg l ⁻¹)
1	36	27400	0.45	116	3*	0,5,10,15,20,25	-	17	35	23	2040
2	15	11000	0.45	18	9	0,5,10,15,20,25	0,4,8,12	3	37.6	20	9600
3	21	8200	0.45	23	12	0,5,10,15,20,25	0,4,8,12,16	4	35.2	20.5	13000

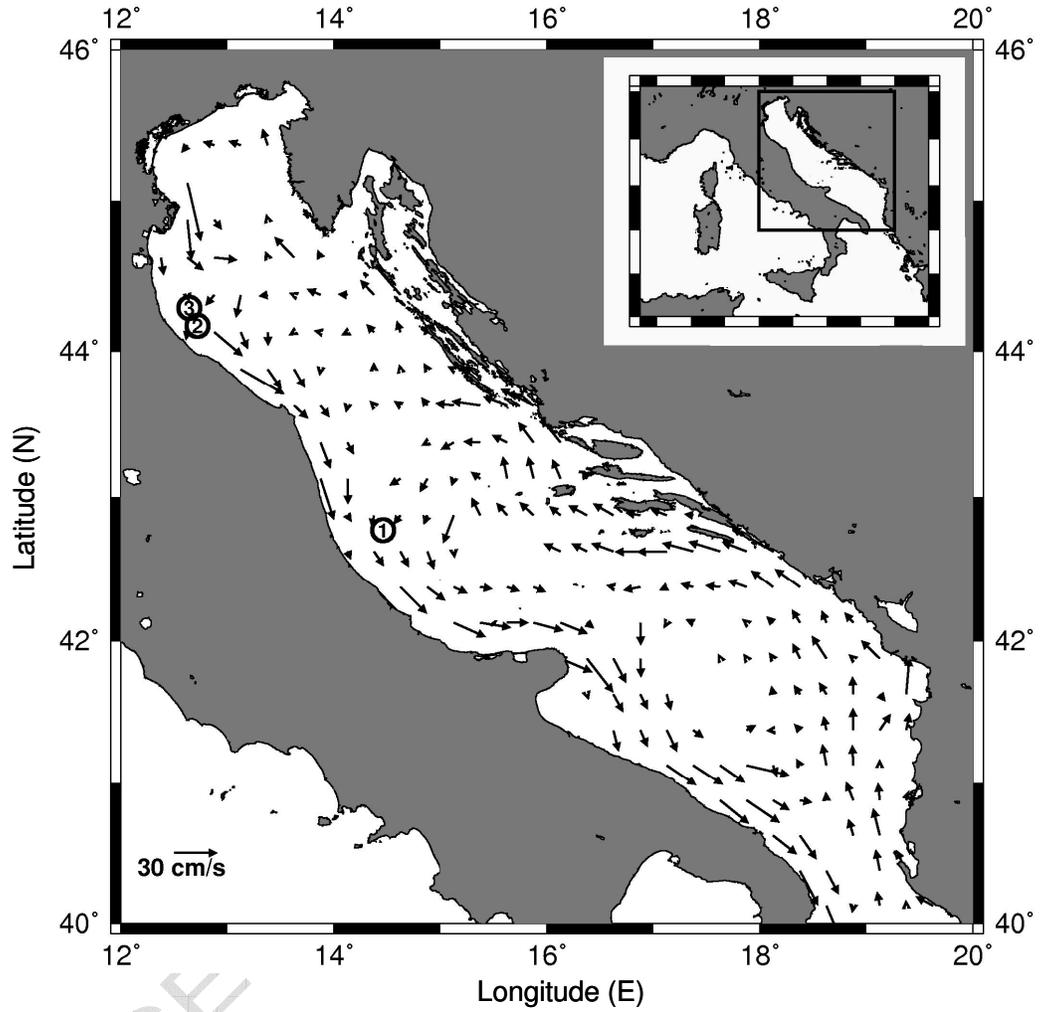
* Outfall located above sea surface

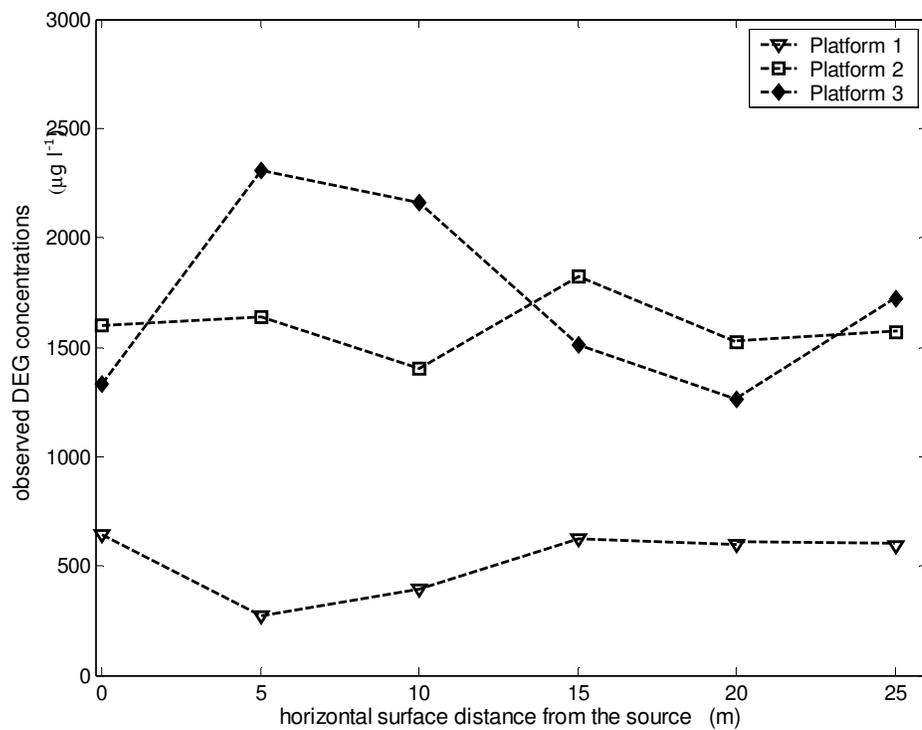
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4Table II
Output model values

Platform	Length of initial mixing zone	Trap level depth	Plume thickness	Froude number	Effluent density	Ambient density	N Frequency	Depth Max rise/fall	Near field dilution S_a	Initial Dilution time
	(m)	(m)	(m)		(σ_t)	(σ_t)	(rad s^{-1})	(m)		(s)
Summer DEG										
1	15.0	Surface	0.5	0.16	23.95	25.75	0.0758	surface	175	90
2	2.3	9.8	1.4	0.66	26.73	24.80	0.3380	10.0	55	70
3	14.8	11.5	1.3	0.15	24.80	25.02	0.3326	11.3	74	400
Winter PFW										
1	10.0	Surface	1.2	0.09	23.95	29.00	0.0919	surface	170	60
2	6.8	7.8	1.7	0.06	26.73	27.78	0.1539	7.5	135	185
3	6.7	10.8	2.2	0.03	24.80	26.50	0.2323	10.5	200	150

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Fig. 1

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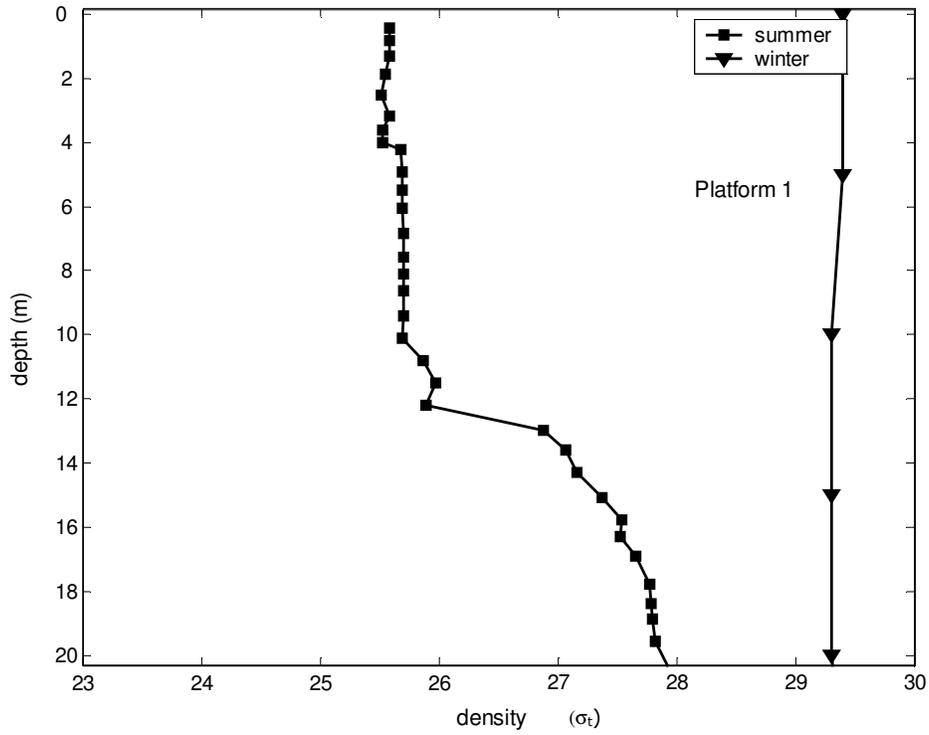
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Fig. 3a

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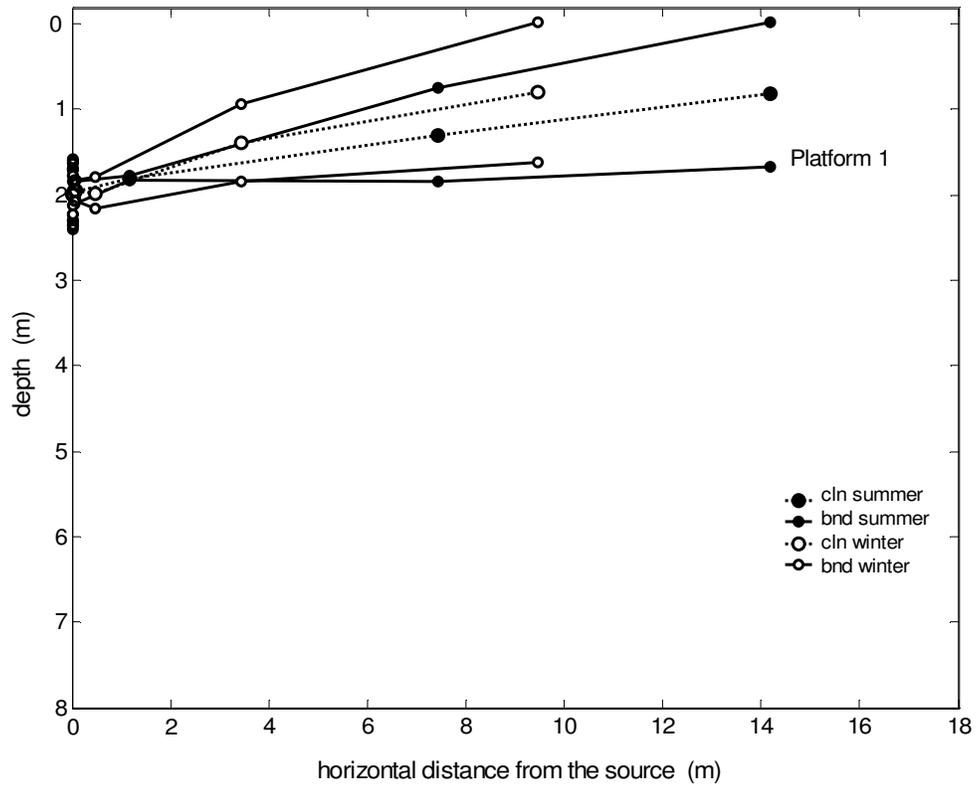


Fig. 3b

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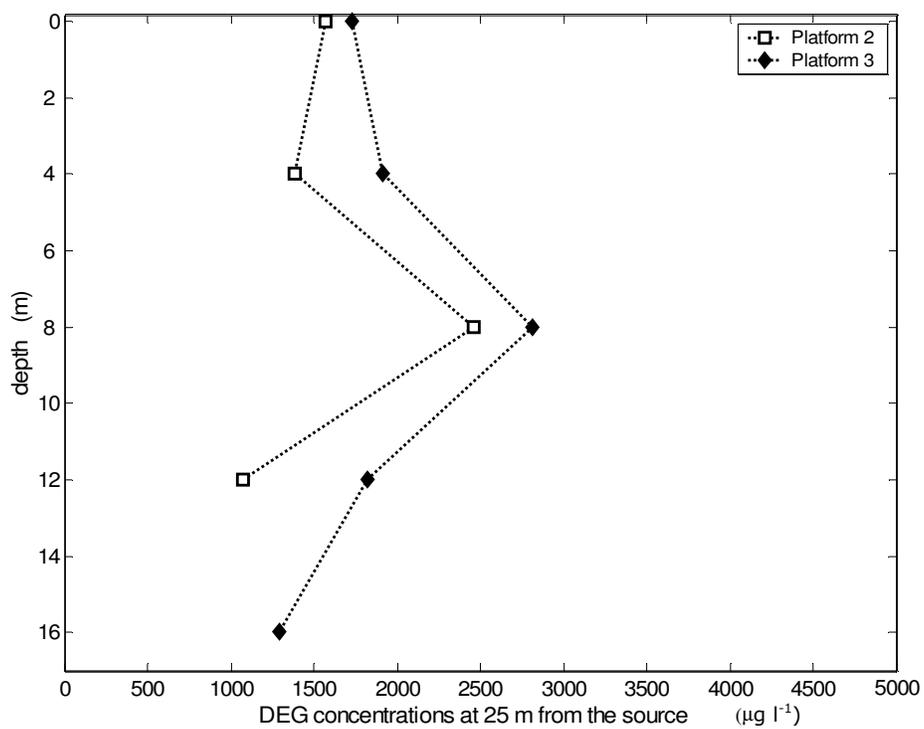
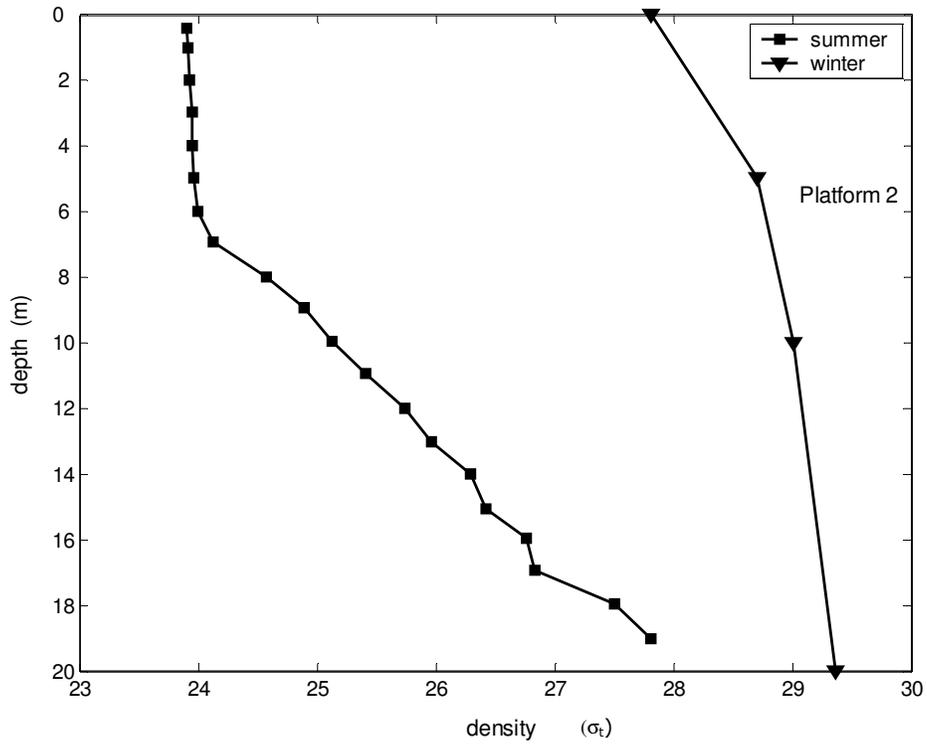


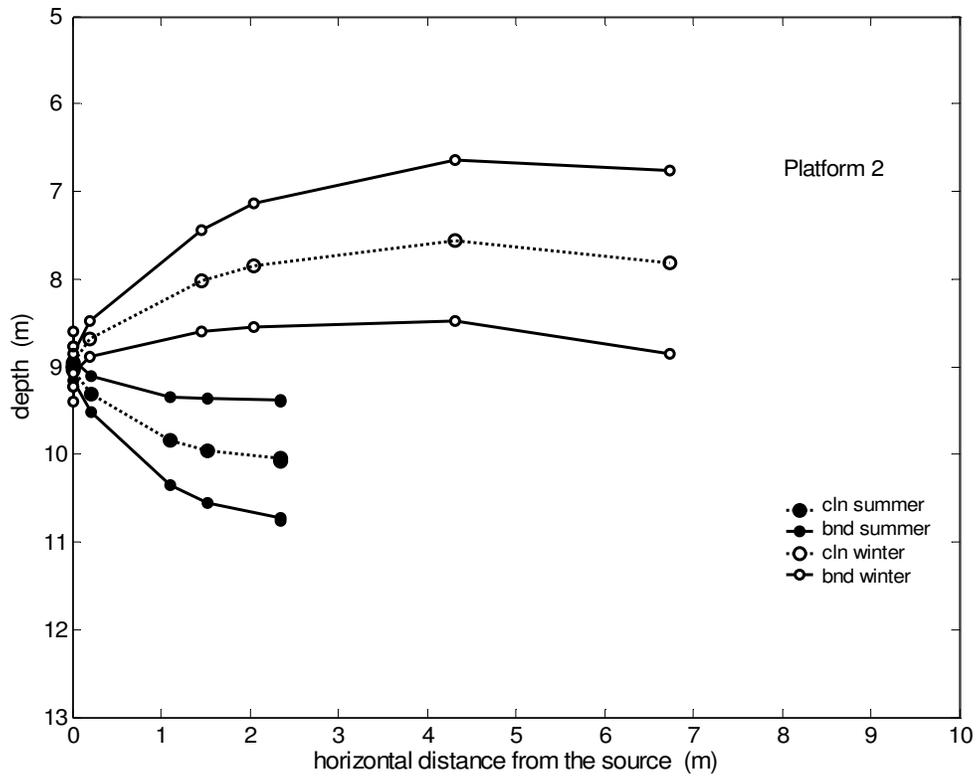
Fig. 4

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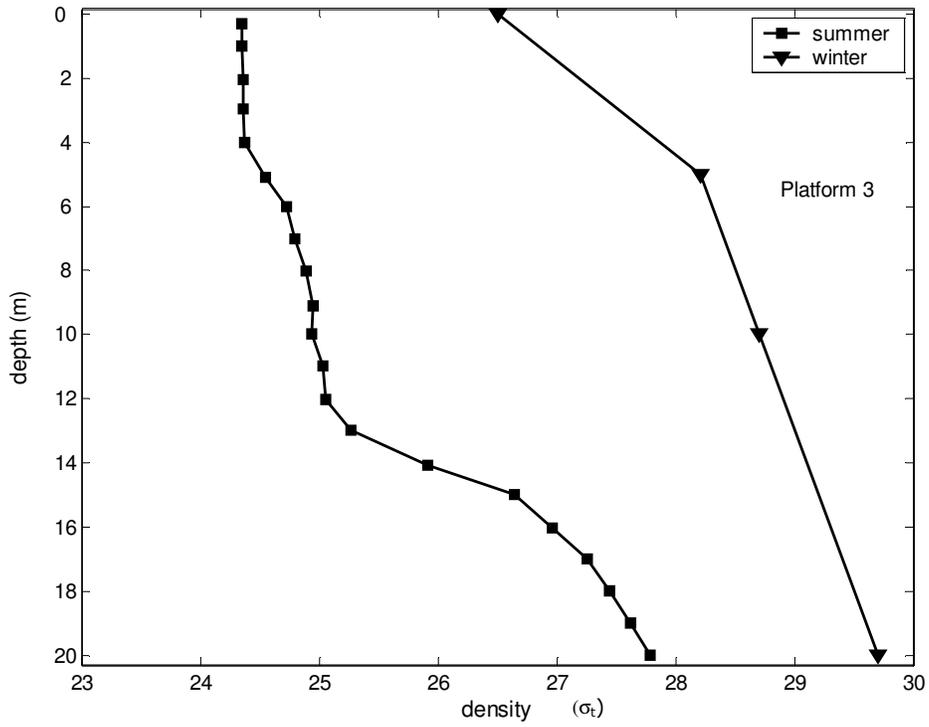
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Fig. 5a



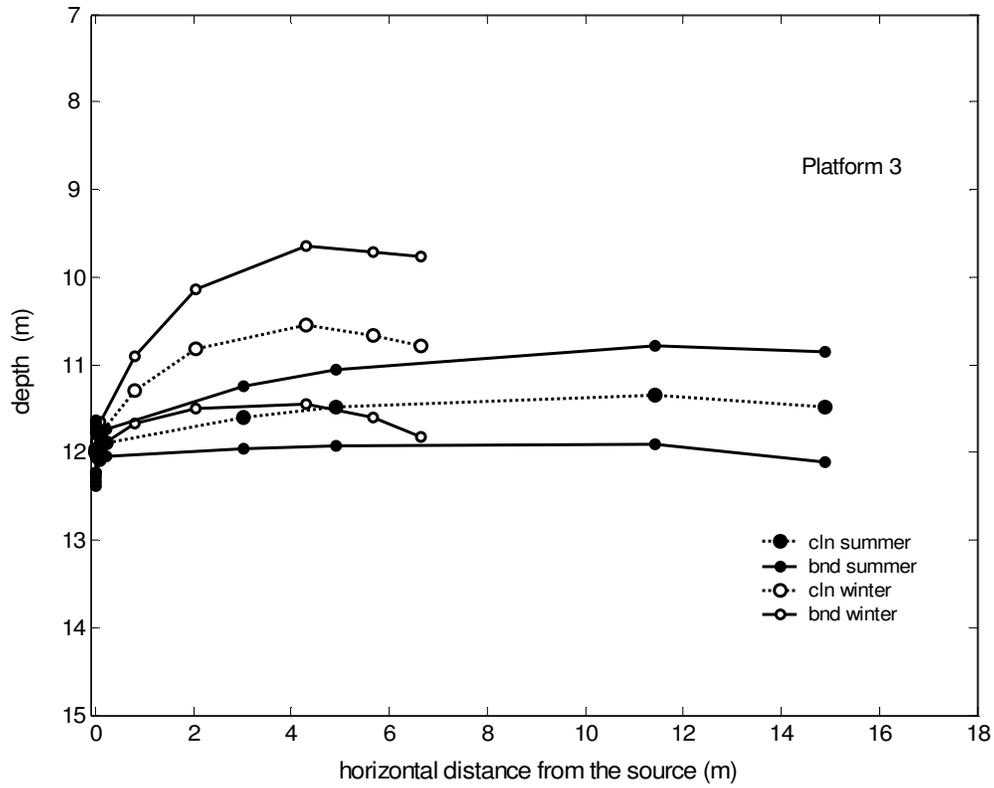
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Fig. 5b



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Fig. 6a



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Fig. 6b