Onderzoeksopdracht DG5/INSPA/RMa23.160 met betrekking tot de Paardenmarkt, een stortplaats voor munitie uit W.O.-I:

Aanbevelingen betreffende chemische monitoring

EINDRAPPORT
FINAL REPORT

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Inleiding

Sinds een aantal jaar wordt op de Paardenmarkt, een oude munitiestortplaats uit W.O.-I voor de Belgische kust, op regelmatige tijdstippen een chemische monitoring uitgevoerd in opdracht van de federale diensten van het leefmilieu. In totaal werden zo al 9 staalnamecampagnes uitgevoerd. Sediment- en waterstalen werden onderzocht naar de aanwezigheid van een of meerdere toxische strijdmiddelen (Yperiet, Clark, TNT en hun afbraakproducten). Op slechts 1 lokatie werd de aanwezigheid van Yperiet aangetoond (in 1996). Behalve dit ene geval, leek de analyse van de sediment- en waterstalen nergens duidelijke aanwijzingen te geven voor toxische verontreiniging. Ook werden er geen opvallende concentraties aan zware metalen gemeten.

De resulaten van deze chemische monitoring moeten echter met de nodige voorzichtigheid genomen worden. Uit de rapportage bleek namelijk dat de staalname, staalvoorbereiding en analysetechnieken niet waren aangepast aan de specifieke omstandigheden en het buitengewoon karakter van de Paardenmarkt. Er was weinig informatie bekend m.b.t. de gebruikte detectielimieten, en de kans is groot dat deze limieten te hoog lagen om de verwachte toxische concentraties te kunnen detecteren. Daarnaast waren de gebruikt extractie- en analysemethode niet steeds optimaal voor de detectie van de toxische strijdmiddelen in kwestie (zeker wat betreft arseenverbindingen). Hieruit blijkt dat er momenteel nood is aan duidelijke richtlijnen met betrekking tot de staalnames en de hieraan verbonden chemische analyse van sediment- en waterstalen. Deze studie wil daaraan tegemoet komen.

Doelstellingen

Doelstelling van deze studie is het maken van aanbevelingen met betrekking tot chemische monitoring van de Paardenmarkt. Deze opdracht wil een antwoord geven op volgende vragen:

- Hoe worden de stalen het best genomen?
- Hoe worden de positionering van de stalen, het voorbereiden van de stalen, de staalbewaring en het vervoer van de stalen het best uitgevoerd?
- Wie kan deze stalen nemen, en wat is de geschatte kostprijs ?
- Welke zijn de analysetechnieken die het best worden aangewend voor kwalitatief en kwantitatief onderzoek?
- Wie kan deze analyse uitvoeren, en wat is de geschatte kostprijs?

Voor deze studie werd zeer nauw samengewerkt met de Finse subcontractor VERIFIN (‘Finnish Institute for Verification of the Chemical Weapons Convention’).

Om praktische redenen werd ervoor gekozen om het rapport in het engels op te stellen. Een uitgebreide samenvatting werd voorzien in het Nederlands (p 37-41).

Task 1.1. Procedures and guidelines for positioning of the samples

In order to allow highly accurate positioning of the sampling locations different aspects need to be considered such as the available geophysical and topographical data, and the latest available (underwater) positioning technology.

1.1.1. Location and distribution of the sampling sites

The choice for the optimal location of sampling sites at the Paardenmarkt will depend on the available, most recent information regarding (1) the distribution of the munition (information obtained from magnetic/gradiometric investigations), (2) the depth below the sea floor of the munition (information obtained from magnetic and/or gradiometric investigations), (3) the topography of the sea floor (information obtained from multibeam investigations), and (4) the dispersion of the toxic elements in the sediments and sea water (information obtained from modelling studies).

The most recent magnetic/gradiometric measurements were carried out in 2012. However at this moment no report is yet available of this study (this is expected in spring 2013). We will therefore base our assumptions on the results of the 1998 study “Magnetometrisch onderzoek op de Paardenmarkt”, carried out by the University of Liège, and the 2005 study “Uitvoeren van gevorderde magneto/gradiometrische metingen op testzones op de Paardenmarkt” (INSPA-22701), carried out by G-Tec. The results of this study were the following:

- Distribution of the munition: two different zones can be distinguished, (1) a central zone with a high density of large magnetic anomalies, and (2) a large surrounding zone with smaller and less frequent anomalies;
- In 2005 a test zone of 100m x 1km was investigated, within this test zone a large central magnetic cluster containing roughly 350 objects was identified;
- Mass: most objects (or clusters of objects) in the central zone have a mass less than 200 kg;
- Horizontal precision: horizontal positions (x, y) of buried objects can be obtained with 1 m resolution;
- Vertical precision: the burial depth remains inaccurate due to uncertainties regarding the geometry and the magnetic characteristics of the objects. Rough estimates indicate that most object seem to be located 2 to 6 m below the seafloor;
- Geometry: a clear distinction can be made between singular objects and clusters of objects, as well as the form of the object (e.g. elongated, circular, …).
- Extrapolation of the mass calculation to the entire dumpsite reveals that a large part of the buried munition was apparently not detected. Most likely it concerns individual shells that are too small for detection, or small clusters buried too deep for detection.

Multibeam and side-scan sonar investigations were carried out by Magelas in 2003 (INS-22665), 2005 (INS-22700), 2008 (INS-23101) and 2011 (INS-10016). The results indicate that there is no munition present at the sea floor. The seabed sediments consist mainly of fine grained sand. The sediment distribution seems to be stable throughout the last years. Silt and mud occur towards the southwest, with the mud content increasing towards the south. The seafloor topography is quite flat. Towards the south megaripples and small sand waves (< 0.5 m high) occur locally, which are most likely related to storms. In 2011 the water depth ranged between 1 and 5 meter (with respect to the mean lowest low water level).

Regarding the topographic evolution of the dumpsite the following conclusions can be drawn:

- Between 2008 and 2011 almost the entire dumpsite was subject to slight erosion (between 0.1 and 0.4 m). The most pronounced erosion took place in the southern part. In the central part of the dumpsite, where most of the munition is located, the average erosion was 0.27 cm.
- Between 2003 and 2011 the dumpsite was subject to erosion (up to 0.6 m). The most pronounced erosion was in the central and northeastern part. Slight accretion (10-20cm) took place in the southernmost part.
- Between 1996 and 2011 there is a clear sediment accretion in the southern part and slight erosion in the north.
- The main changes in sediment budget were between 1996 and 3003. Since 2003 there seems to be a relative equilibrium with minor (periodic) changes in the sediment budget.

In order to allow a correct sampling strategy, also the spreading of the contamination away from the munition shells must be taken into account. In recent years three different dispersion studies were carried out by MUMM, respectively with regard to Yperite (INS-22472, in 2003), Clark (INS-23059, in 2006) and TNT (INS-23032, in 2007). The results of these dispersion studies indicate the following:

- The dispersion of Clark from a buried shell in sediment will likely be less than 0.5 m in 10 years, and 1.5 m in 100 years. Acute contamination of Clark in the water column can most likely be ruled out. However minor contamination is possible.
- The dispersion of Yperite from a buried shell in sediment is expected to remain limited to a volume of sediment smaller than the volume of the shell itself. Significant contamination of Yperite in the water column is expected within a radius of 40 cm from the leaking shell. Minor contamination is however possible further away from the shell.
- The dispersion of TNT from a buried shell in sediment will probably be confined to some 10 cm around the shell. Acute contamination of TNT in the water column can most likely be ruled out. However minor contamination is possible.

Based on the results from the magnetic/gradiometric investigations, the topographic studies and the dispersion models the following plan is proposed regarding the sampling locations:

- *In total between 20 and 30 sampling locations within the dumpsite.*
- *Location and distribution of sampling points: this will be based on the results from the most recent gradiometric study (2012-2013). The majority of the sampling points should lie in the central part of the dumpsite where the largest and most frequent magnetic anomalies were observed. The sampling points should for a large part focus on large magnetic anomalies at shallow depth, but in addition also smaller and/or deeper magnetic anomalies should be targeted, as well as anomaly-free areas (which could equally contain buried munition).*
- *Between 2 and 5 reference locations outside dumpsite in order to guarantee that the samples taken from these sites are clean.*
- *Location and distribution of the reference points: these can be chosen at random within a range of a few hundred meters to 1 km outside the dumpsite.*
- *In case of positive results, new sampling should be performed at the exact same spot.*
- *The sampling locations should not remain the same for each sampling campaign. This is needed in order to increase the coverage of the sampling map. Those locations that contain chemical warfare agents should be monitored for a long-term evaluation, in other words in each sampling campaign. It is advised that also certain target locations (e.g. large magnetic anomalies at very shallow depth) should be monitored on a regular basis.*

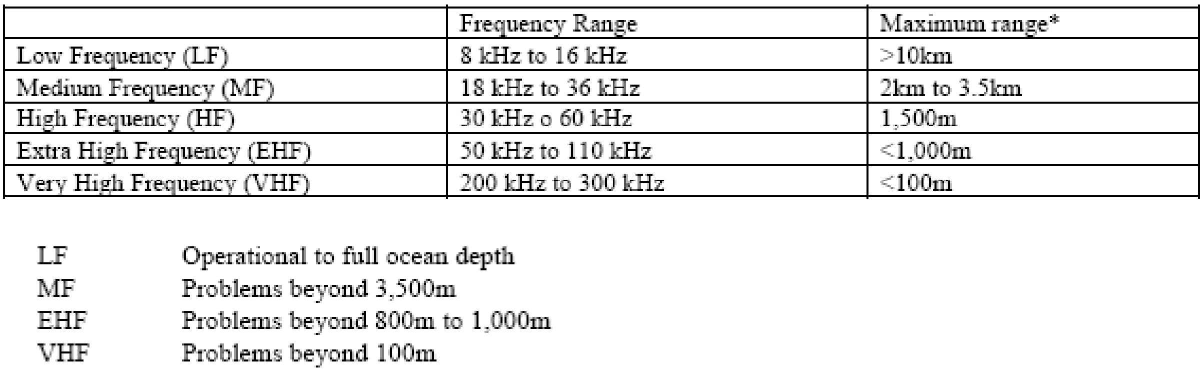
Positioning accuracy

The positioning accuracy of the sampling locations will to a large extent determine the success of the sampling. Keeping in mind the limited size of the contaminated area around the leaking munition (as discussed in 1.1.1), the sampling operations at the Paardenmarkt require *a positioning accuracy in the sub-meter range*. This poses major technological challenges in underwater positioning. Above water correct positioning with cm and dm resolution is not a problem thanks to DGPS and related RTK tracking. For subsea operations however this becomes a different story because GPS employs radio signals that do not propagate underwater.

Accurate positioning underwater of the sampling sites can be done using different techniques. Most of these techniques are based on acoustic positioning systems. In the next chapters these techniques will be discussed in detail, as well as their advantages and disadvantages and practical aspects with regard to the specific case of the Paardenmarkt.

In general three systems of underwater acoustic positioning are recognized: long-baseline systems (LBL), short-baseline systems (SBL), and ultra-short baseline systems (USBL). Recently also a fourth system has become widely used, the GPS intelligent buoys system (GIB). All these systems measure positions relative to (one or more) baseline station(s), which must be deployed prior to operations. Acoustic positioning systems can yield an accuracy of a few centimeters to tens of meters, depending on the system and the frequency band that is used, and can be used over operating distance from tens of meters to tens of kilometers. The performance depends strongly on the type and model of the positioning system, its configuration, and the characteristics of the underwater acoustic environment at the work site.

The table below lists the different frequency bands commonly used for acoustic positioning systems.



	Frequency Range	Maximum range*
Low Frequency (LF)	8 kHz to 16 kHz	>10km
Medium Frequency (MF)	18 kHz to 36 kHz	2km to 3.5km
High Frequency (HF)	30 kHz o 60 kHz	1,500m
Extra High Frequency (EHF)	50 kHz to 110 kHz	<1,000m
Very High Frequency (VHF)	200 kHz to 300 kHz	<100m

LF	Operational to full ocean depth
MF	Problems beyond 3,500m
EHF	Problems beyond 800m to 1,000m
VHF	Problems beyond 100m

However we should not forget that a first and crucial requirement of all underwater acoustic positioning systems is the accuracy of the overall GPS system (on the vessel). The latter should be of the highest possible accuracy, i.e. at least in the decimeter or centimeter range. For the Paardenmarkt the best approach is to use RTK (real-time kinematic) positioning, which is a realistic option in view of the vicinity of the dumpsite to the coast. The new Flemish research vessel Simon Stevin is equipped with RTK dynamic positioning (unfortunately RV Belgica still lacks RTK). Also a large number of smaller commercial research vessels are equipped with RTK.

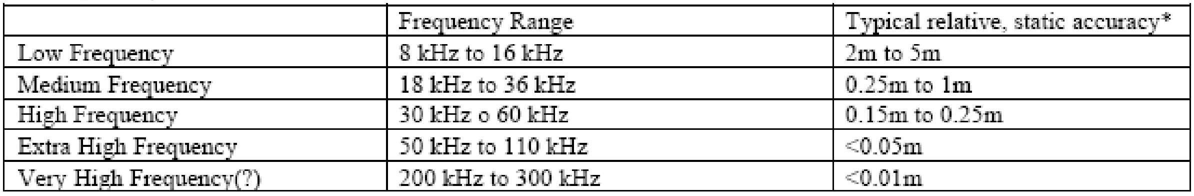
1.1.2. Long-baseline (LBL) systems

LBL systems use a sea-floor baseline transponder network. The transponders are typically mounted in the corners of the operations site. LBL systems yield very high accuracy of generally better than 1 m and sometimes up to a few cm with very robust positions. The high accuracy is a result of the fact that the transponders are installed in a reference frame on the sea floor, the wide transponder spacing results in an ideal geometry for position computations, and the LBL system operates without an acoustic path to the (potentially distant) sea surface. The baseline transponders of LBL systems are typically mounted in the corners of an underwater work site within which the diver operates. In this case, this means they would be mounted at the corners of the Paardenmarkt dumpsite.

Operation: Long baseline systems determine the position of diver (or a vehicle) by acoustically measuring the distance from the diver to three or more baseline transponders on the seafloor. These range measurements are used to triangulate the position of the diver. The resulting position however is relative to the location of the baseline transducers, and can be converted to a geo-referenced coordinate system (e.g. latitude/longitude, UTM) using the geo-positions of the baseline stations. Unlike SBL or USBL systems there is no need for converting between reference frames. Furthermore seafloor mounting makes the positioning accuracy independent of water depth.

Figure 1. *Principle of long-baseline (LBL) underwater positioning systems*

The accuracy of conventional LBL systems is independent of water depth but very dependent upon frequency of the transmitted acoustic signal. The following table lists the positioning accuracy versus frequency:



	Frequency Range	Typical relative, static accuracy*
Low Frequency	8 kHz to 16 kHz	2m to 5m
Medium Frequency	18 kHz to 36 kHz	0.25m to 1m
High Frequency	30 kHz o 60 kHz	0.15m to 0.25m
Extra High Frequency	50 kHz to 110 kHz	<0.05m
Very High Frequency(?)	200 kHz to 300 kHz	<0.01m

Positioning accuracy versus frequency for Long-baseline (LBL) acoustic positioning systems

Note: Static accuracy applies to a static sampled (multiple acoustic observations in the same place) accuracy. Most likely the accuracy for dynamic moving objects such as divers (with a single position update per location up to 3 or 4 seconds) is (much) less than this.

Advantages of LBL positioning systems:

- Very high positioning accuracy, independent of depth and range (1 meter or less);
- You don't need a compass or gyro;
- Only small transducer are needed (only one deployment machine/pole).

Disadvantages of LBL positioning systems:

- The system is complex and requires expert operators;
- It involves large arrays of expensive equipment;
- It involves considerable operational time consumed for deployment/recovery;
- Each deployment requires comprehensive calibration;
- Recuperation of the transponders is not straightforward.

Manufacturers:

- Sonardyne - Fusion LBL, Prospector LBL (www.sonardyne.com/products/positioning)
- Kongsberg - HiPAP, HPR400P (www.km.kongsberg.com/ks/web/nokbg0240.nsf/AllWeb/FF57C18363FAD917C1256A7E002B9F2F?OpenDocument)
- EvoLogics - S2CR LBL (www.evologics.de/en/products/LBL/index.html)
- Desert Star - Aquamap Seafloor, Rangenav (www.desertstar.com/Products_category.aspx?intProductCategoryID=4)
- LinkQuest – Pinpoint (www.link-quest.com/html/lbl_intro.htm)

Conclusion

Notwithstanding the high positioning accuracy that can be obtained with the Long-baseline (LBL) system, it is not recommended for the Paardenmarkt due to (1) the complexity (large arrays, complex calibration), (2) expensive equipment involved (multiple baseline stations), and (3) high currents at the dumpsite (making seafloor mounted transponders very tricky).

1.1.3. Short-baseline (SBL) systems

SBL systems use a baseline consisting of three or more transducers that are connected to a central control box. The accuracy depends on the transducer spacing and the mounting method. When a wider spacing is employed (e.g. when working from a large platform), the performance can be similar to long-baseline (LBL) systems. When operating from a small boat where transducer spacing is tight, accuracy is reduced. Like ultra-short baseline (USBL) systems, SBL systems are frequently mounted on boats and ships.

Operation: Short baseline systems determine the position of a tracked target, such as a diver, by measuring the target's distance from three or more transducers that are typically lowered over the side of a surface vessel or fixed platform. These range measurements are used to triangulate the position of the target. The resulting target positions are always relative to the location of the baseline transducers. A GPS receiver and electronic compass mounted on the boat/platform determine the location and orientation of the latter, which is then combined with the relative position data from the SBL system to establish the geo-referenced position of the diver (e.g. latitude/longitude, UTM).

Short baseline systems get their name from the fact that the spacing of the baseline transducers is usually much less than the distance to the target, e.g. a diver venturing far from the boat. As with any acoustic positioning system, a larger baseline yields better positioning accuracy. When operating from larger ships or platforms (where greater transducer spacing can be used) SBL systems can yield a positioning accuracy around 1 meter.

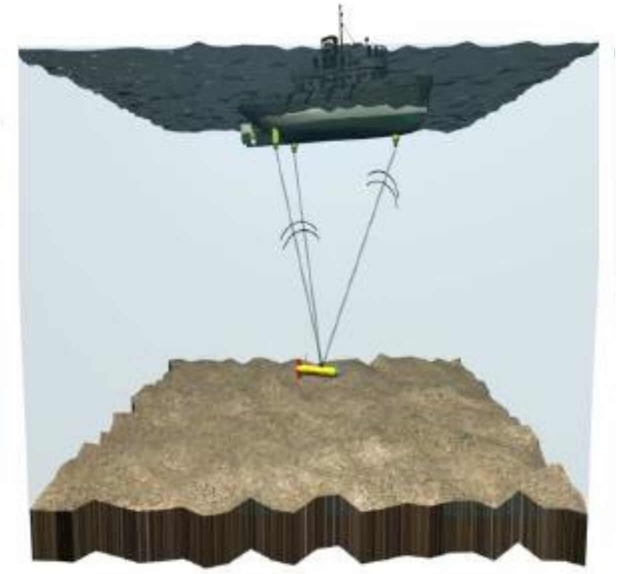


Figure 2. *Principle of short-baseline (SBL) underwater positioning systems*

Advantages of SBL positioning systems:

- Lower system complexity than LBL makes SBL a relatively easy tool to use;
- Good update rate when used with a pinger instead of transponder;
- Spatial redundancy built in;
- Ship based system – no need to deploy transponders on the seafloor;
- Small transducers/gate values.

Disadvantages of SBL positioning systems:

- Very good dry dock/structure calibration required;
- Detailed offshore calibration of system required;
- Lower position accuracy than for LBL systems that will depend on additional sensors (gyro and vertical reference unit);
- >3 transceiver deployment poles/machines needed.

Manufacturers:

- Kongsberg - HiPAP system, HPR400P system (www.km.kongsberg.com/ks/web/nokbg0240.nsf/AllWeb/FF57C18363FAD917C1256A7E002B9F2F?OpenDocument)
- Desert Star - PILOT LBL (www.desertstar.com/Products_product.aspx?intProductID=1)

Conclusion
In view of the relatively low accuracy (> 1m), the difficult calibration and the large number of transponder poles involved, the Short-baseline (SBL) system is not recommended for the Paardenmarkt.

1.1.4. Ultra-short-baseline (USBL) system

USBL underwater positioning systems rely on a small transducer array (so-called transceiver) that is typically mounted on a pole below a surface vessel. The subsea responder can either be held by a diver or installed on the seafloor or on a ROV. An acoustic pulse is transmitted by the transceiver and detected by the subsea transponder, which replies with its own acoustic pulse. To calculate a subsea position, the USBL calculates both the range and angle from the transceiver to the subsea receiver. Angles are measured by the array of transducer array which normally contains three or more transducers separated by a baseline of 10 cm or less. Using the phase of the transducer array allows to calculate the angle to the subsea transponder.

Figure 3. *Principle of ultra-short-baseline (USBL) underwater positioning systems*

The combination of distance and direction fixes the position of the tracked target relative to the surface vessel. Additional sensors such as GPS, a gyro or electronic compass and a vertical reference unit are then used to compensate for the changing position and orientation (pitch, roll, bearing) of the surface vessel and its transducer pole.

USBL systems offer the advantage of not requiring a sea floor transponder array such as the LBL systems. Furthermore they are easy to use (only a single transceiver at the surface). The disadvantage is that positioning accuracy and robustness are sometimes not as good as for LBL systems. This is due to (1) an increase of the positioning error with distance (however for relatively small distances, such as the case for the Paardenmarkt, this error will remain small) and (2) additional errors introduced by multiple sensors needed for the USBL transducer pole position and orientation. Furthermore the transducer pole may require a high degree of repeatability of alignment. The latter is however avoided with the new GAPS USBL system where the attitude sensors and transducer head are included in one system (no separate offsets to be measured) thus avoiding time-consuming calibration.

The accuracy and repeatability of the current USBL systems is generally quoted as a percentage of the slant range (i.e.3D distance between the diver and the baseline transponder on the sea floor). This means that the greater the depth - the greater the slant range - the less repeatable the position. Typically numbers of percentage are 0.2 and 0.5%, depending on the used frequency. For a slant distance of 1 km this would imply an accuracy between 2 and 5 meter (at its best). For a distance of 300 meter, which is a realistic assumption for the Paardenmarkt, this would imply an accuracy roughly 0.5 - 1 meter.

Advantages of USBL positioning systems:

- Low system complexity makes it an easy tool to use;
- Ship based system – no need to deploy a transponder array on the seafloor;
- Only a single transceiver at the surface – one pole/deployment machine;
- Good range accuracy with time of flight systems.

Disadvantages of USBL positioning systems:

- Detailed calibration of the system required (this is not the case for the GAPS USBL);
- Position accuracy generally lower than for LBL systems;
- Transducer pole requires detailed (time-consuming) calibration (the latter is not the case for the GAPS USBL);
- Decrease of data quality in shallow water, due to multiple reflections from the water surface and water bottom (this is not the case for the latest GAPS USBL)

Manufacturers:

- IXSEA - GAPS USBL (www.ixsea.com/en/subsea_positioning/1/gaps.html)
- Sonardyne – Ranger 1/2 USBL, Scout USBL (www.sonardyne.com/products/positioning/usbl-all-systems.html)
- Applied Acoustics – EASYTRAK (www.appliedacoustics.com/easytrak-usbl-systems)
- LinkQuest - TrackLink (www.link-quest.com/html/intro2.htm)
- Tritech – MicronNav (www.tritech.co.uk/product/usbl-tracking-system-micronnav)
- Kongsberg – HiPAP, HPR400P (www.km.kongsberg.com/ks/web/nokbg0240.nsf/AllWeb/FF57C18363FAD917C1256A7E002B9F2F?OpenDocument)
- EvoLogics – S2CR USBL (www.evologics.de/en/products/acoustics/S2CR_USBL_Modem.html)

Figure 4. *The GAPS USBL system lowered over the side of the ship*

Conclusion

In view of the high positioning accuracy (~1m for distances up to a few hundred meter) and the simplicity of the system (transducers/sensors combined in one housing, fast initialization and calibration) the USBL system, and in specific the GAPS USBL system, seems to be a suitable option for the Paardenmarkt. A possible drawback is the high price of the GAPS system (in the order of 200.000 USD, excluding VAT). However this can be overcome by using the GAPS system that has recently been acquired by VLIZ (Vlaams Instituut voor de Zee), and made available free of charge for the scientific community. The compact size of the GAPS system (diameter 30 cm, height 65 cm) allows its use both on larger vessels (e.g. Simon Stevin) but also on small vessels (< 10 m).

1.1.5. GPS intelligent buoys (GIB) systems

GPS intelligent buoys (GIB) systems are “inverted” LBL devices where the transponders on the sea floor are replaced by floating buoys, self-positioned by GPS. The tracked position is calculated in real time at the surface from the arrival times of the acoustic signals sent by the underwater device (e.g. diver) and acquired by the buoys. This configuration allows fast, calibration-free deployment with an accuracy similar to LBL systems. Unlike LBL, SBL or USBL systems, GIB systems use one-way acoustic signals from the emitter to the buoys, making it less sensible to surface (or wall) reflections.

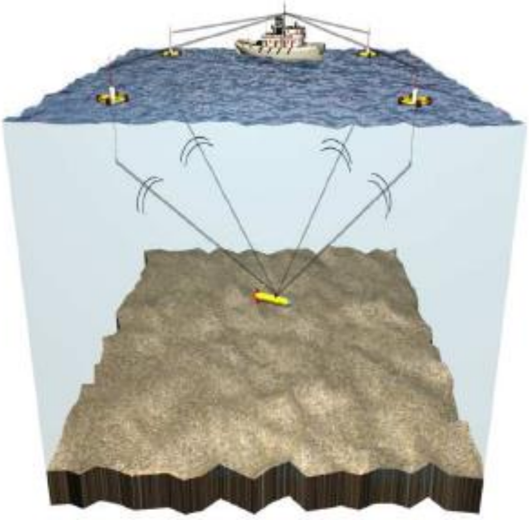


Figure 5. *Principle of GPS intelligent buoys (GIB) underwater positioning systems*

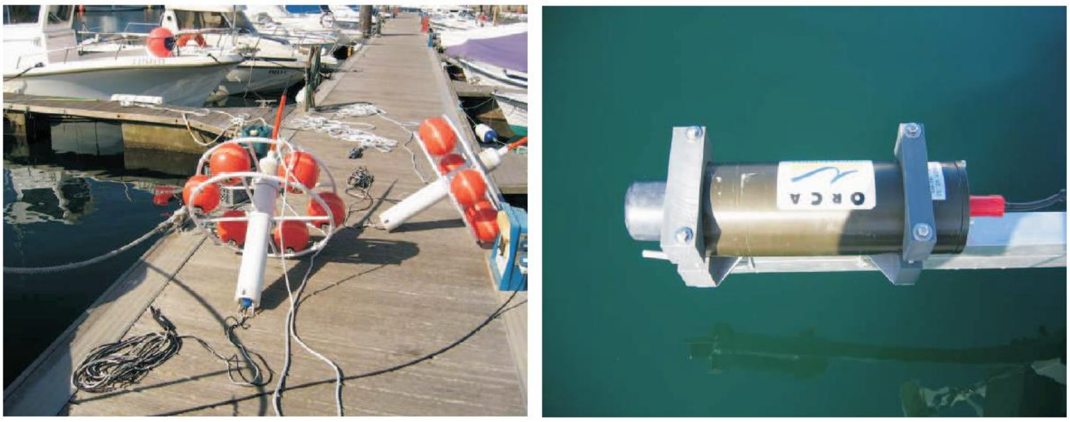


Figure 6. *Left: GIB buoys before deployment. Right: GIB pinger.*

The GIB system is patent protected and products are manufactured by the French company ACSA-underwater-GPS (subsidiary of the ALCEN group). Three off-the shelf products are available: the small portable GIB-Lite system, the large torpedo tracking GIB-FT system, and the medium-range GIB-Plus system.

Advantages of the GIB positioning system:
- High positioning accuracy (dm accuracy in shallow water);
- Small transponders that are easily recuperated;
- Easy and fast installation (limited calibration);
- High rate of positioning update (1Hz)

Disadvantages of the GIB positioning system:
- The equipment is expensive;
- The use of buoys may be problematic in areas with high currents (drifting buoys);

Manufacturers:
ACSA – GIB-Lite/GIB-FT/GIB-Plus/GIB-SAR (www.acsa-alcen.com/positioning-acoustics)

Conclusion
The high positioning accuracy makes the GPS intelligent buoys (GIB) system appropriate for the envisaged sampling surveys. However major drawbacks of the positioning system are (1) the high costs involved, and (2) the high currents that may cause the buoys to drift. In view of these drawbacks the GIB system is not recommended for the Paardenmarkt.

1.1.6. Non-acoustic systems: Smart Tether underwater positioning

The Smart Tether underwater positioning system is a completely non-acoustic system. It uses orientation sensors housed within a tether (i.e. cable) that is connected to the diver and does not need to communicate with any external hardware. Therefore it is not prone to problems with acoustic reflections, noise, or obstructions. The cable has a diameter of 5 mm and its working distance is roughly 120 m.

Figure 7. *Left: Smart Tether sensor node. Right: Smart Tether system (cable, screen)*

The Smart Tether is based on the Doppler principle and uses orientation and depth sensors at multiple locations along the tether. Using the data from these sensors, the shape of the tether can be determined, and thereby the position of the diver relative to the operator (who is stationed on board of the vessel). The operator's absolute location can be determined e.g. by a DGPS or RTK antenna. By adding the diver's relative position to the operator's absolute position, the diver's absolute real-time position is determined. The update rate is 5 seconds. The positioning accuracy of the diver can be extremely good, sometimes even in the centimetre range.

Advantages of Smart Tether system:

- High positioning accuracy;
- Non-acoustic system so no noise problems;
- Cable allows direct communication with the diver;

Disadvantages of Smart Tether system:

- Since the Smart Tether system involves calculation of the diver's position based the acceleration relative to water, the positioning error may become quite large (meter-range) in the case of (relatively) strong water currents.
- The diver is connected by a cable to the operator on board the ship which may affect the performance of the diver;
- Limited working range.

Manufacturers:
KCF - Smart Tether (www.smarttether.com)

Conclusion
The Smart Tether system is a relatively simple system but still has some major drawbacks which make it not entirely appropriate for sampling surveys at the Paardenmarkt dumpsite.

1.1.7. Diver navigation boards

Diver navigation boards are small hand-held platforms which allow a diver to navigate underwater autonomously like a surface based GPS receiver. The board often weighs around 2-3 kg and is relatively easy to operate. Sealed housing provides protection for all internal components and rechargeable batteries allow continuous operated for several hours. Most boards supply geodetic position, depth and heading. In some cases the diver's position is plotted and updated on a LCD display in real time. A dive plan, including waypoints and routes to navigate to, can be uploaded. Underwater, the bearing and distance to selected waypoints can be displayed on the screen along. In some cases a retractable antenna is deployed for position updates.

Navigation boards have successfully been used in lakes and clear water environments. The main drawback of the navigation boards is the positioning accuracy – this is often in the range of 3 meters or less. An additional drawback is the high current and low visibility at the dumpsite, which make the navigation board difficult to use. Since the position calculation is based on velocity from Doppler Velocity Log (DVL) and heading from compass, the accuracy will be problematic in high current environments.

Advantages of diver navigation boards:

- Easy to use;
- The diver has information about his real-time position;
- No cable needed;

Disadvantages of diver navigation boards:

- Low positioning accuracy;
- Even lower positioning accuracy in case of relatively strong currents;
- The hand-held board limits the freedom of the diver (who also carries sampling equipment);

Manufacturers:

- DNC - 250 Diver Navigation Platform (www.rjeint.com/diverNav.htm)
- OMG Diver Navigation (www.omg-italy.it/uk/prodotti/sp-plancetta.html)
- RJE International - TAC-series (www.rjeint.com/diverNav.htm)
- AMRON (www.amronintl.com/amron-international-dnb-diver-navigation-board.html)

Conclusion

In view of the listed disadvantages diver navigation boards do not seem to be an efficient option for the Paardenmarkt sampling surveys.

1.1.8. Practical considerations

As we have seen in the previous chapters there are several solutions to tackle the positioning requirements. A number of underwater positioning systems allow to calculate the real-time dynamic position of the diver (who carries a transponder) with sufficient accuracy (1m or sometimes less). Position update rates of 1s (or less) also assure accurate tracking. Using post-processing algorithms the positioning accuracy can in most cases be further upgraded to a decimeter range.

However, the main challenge for the sampling surveys at the Paardenmarkt is the following: *how does the diver know where he is, and how can the diver locate the precise sampling location?* An acoustic transponder carried by the diver, or in the case of Smart Tether a cable connected to the operator/vessel, will supply accurate positioning information to the shipboard computer, but this information is not automatically transferred to the diver. In other words, the diver does not know where he is with respect to the sampling location. Diver boards might seem an option but as we have seen above (in section 6), these do not provide sufficient positioning accuracy and furthermore may seriously hinder the diver before and during the sampling operation.

Possible solutions:

(1) One possible solution is to have a direct communication cable between the diver and the shipboard operator. Navigation instructions can then be passed on to the diver as he/she tries to find his way towards the sampling location. In the case of Smart Tether the same cable may be used for communication. However due to the overall poor visibility at the dumpsite and the currents that are often encountered this approach may not always be very practical (i.e. it will be hard for the diver to know where he is going and what is around him). Furthermore it is possible that the regular ‘pinging’ of the transponder may hinder a clear communication with the diver.

(2) A second option is to attach the transponder with a rope onto a heavy load (e.g. small concrete block) and lower the latter onto the seabed from a small vessel located above the sampling location (preferably the vessel would need a small A-frame). As the update of the position of this concrete block is less than one second it is possible to position this load near the theoretical sampling location roughly within 1-2 meter. The diver then descends via the rope to the concrete block.

Before descending, the diver can be told where to position the sample exactly with respect to the concrete block (e.g. 30 cm to the north), since both coordinates are known with great precision. This will finally allow the necessary positioning accuracy for the sampling operation.

(3) A third possible solution is to use a highly advanced diver navigation and sonar imaging system, recently developed for the military (so-called "Shark Marine Navigator", www.sharkmarine.com/products/navigator.htm). The system is aimed specifically at low visibility environments and is used for search and recovery applications, ship hull inspections, etc. that require high precision. The system does not only allow the diver to know his exact position but also guides the diver to a specific target (in our case the sampling location) using sonar imagery. There is no cable involved. The Shark Marine system is unique and unquestionably meets the positioning requirements for the Paardenmarkt, but it has two major drawbacks: (1) the bulkiness of the system is not easy to combine with the sampling operation; and (2) the system is very expensive.

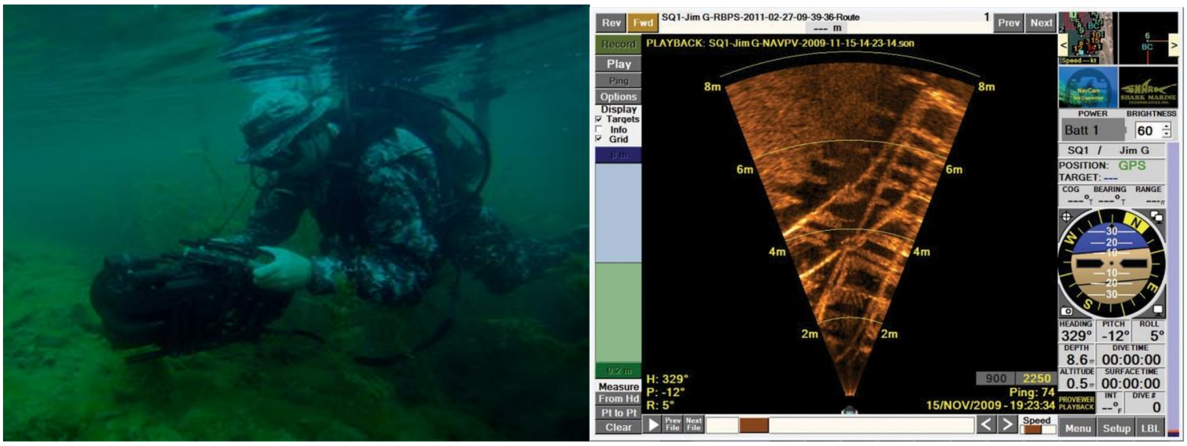


Figure 8. *Shark Marine Navigator system in operation (left) and screen shot with sonar display (right).*

(4) A fourth possible option is to work with a ROV instead of divers. Indeed this would solve the problem of absolute positioning underwater, since it is relatively straightforward to steer the ROV (which has a transponder attached to it) to the precise sampling location. VLIZ (Vlaams Instituut voor de Zee) has a small ROV available that might be used for this purpose. However there are some major drawbacks with this set-up: (1) use of the ROV is labour-intensive and requires a large vessel; (2) accurate navigation of the ROV is tedious in relatively strong currents; and (3) sampling in sandy sediments from a ROV (using a robot arm) is extremely difficult and chances are high that the sampling tube will not fully penetrate the bottom and/or the sediments inside the core will be partially lost.

1.1.10 Conclusions and recommendations

At this moment the best (i.e. most efficient = cost-effective) option seems to be to carry out various in-situ tests with a diver and communication cable (solution 1), and/or with a diver and heavy load (solution 2). In both cases the GAPS USBL system seems most appropriate for positioning of the diver (solution 1) or the concrete load (solution 2). A vessel with small A-frame would be needed for the latter. The outcome of these tests will then allow to determine which approach is best suited for the Paardenmarkt sampling surveys.

Task 1.2. Procedures and guidelines for the sampling itself

1. Number of cores and water samples per sampling location

It is recommended that one sediment core and one water sample is taken at each sampling location. The water sample should be taken just above the seafloor at the exact core location. There is no need for a sample higher up in the water column because of the increased chance of mixing in this upper layer.

The cores and water samples are best stored on board in a freezer at -18°C and transported ready packed to the laboratory carrying out the chemical analysis. This transport should be done within 2 weeks of collecting. Storage temperatures at the laboratory are -18°C for water samples and -18°C for sediment samples.

2. Height of the cores

A core height of 50 cm is proposed. This should be sufficient to monitor the contamination. Deeper cores are difficult to retrieve by hand by the divers.

3. Number of samples per core

In total 2 samples are taken per core: one at the seabed, and a second at the bottom (50 cm depth). Attention: This needs to be done ON BOARD before freezing.

4. Size of the samples

The sediment core samples should be at least 5 cm thick.
Each sediment core sample is divided into sediment and pore water portions. This is done in the lab performing the analysis.

5. Coring tubes

The coring tubes that were used till now on the Paardenmarkt are in plexiglass and stainless steel with pvc caps. In principle this should be ok. A diameter of 5-10 cm is sufficient.

It is very important that good (= full!) cores are obtained, which has not always been the case in the past (quite often half empty cores – or in some cases completely empty cores - were retrieved). In that case it may be better to use a dedicated sand corer that contains a check valve (that can be manually closed by the operator), a stainless steel core body with plastic liner and core catcher, driving tip and extension handles. The sampler can be twisted or hammered into the sediment. The disadvantage is that you would need to decontaminate the core body after each dive.

6. Water samplers

There are two options: (1) the water samples are taken using a Niskin-style sampler. These water samples should then on board be immediately transferred into pre-prepared sample bottles; or (2) the water samples are directly taken with dedicated sample bottles. The second option is preferred since this will avoid possible contamination on board.
The bottles should be stored in a freezer (-18°C) until they are analyzed in the lab.

7. Contamination and safety procedures

Heavy equipment is a risk during sampling activities. Enough free area around the equipment is necessary because of movement of the ship and equipment.

All sampling equipment should be washed and decontaminated before each use to avoid cross-contamination of samples. In general, decontamination procedures for marine field sampling equipment should include (1) scrubbing the equipment with a brush and phosphate free detergent solution (e.g. Alconox™), (2) rinsing with clean site water, (3) rinsing with solvent (hexane, followed by acetone), (4) and rinsing again with clean site water. The solvent rinse should be omitted if the samples are to be analyzed for volatile organic compounds.

The divers taking the core samples should wear a dry suit and rubber gloves. The persons handling the cores on board should wear protective clothing (Tychem F suit), chemical resistant gloves (Nitrile), and protective boots. A gas mask (with active carbon filter) should be at hand. Chemical detectors and detection strips (e.g. multi-IMS detector and CAM+) should also be available on board.

The divers taking the core samples should be informed that cores might contain e.g. polymerized material of Yperite or Adamsite, which still may contain also intact Yperite and Adamsite.

After handling the cores the protective clothing is where needed disinfected (e.g. with domestic bleach) and rinsed with running water. Excess sediment that is not needed for analysis should be collected in dedicated bins on board for later disposal onshore.

The retrieved cores are stored in plastic bottles with detection paper (to detect Yperite). It is suggested not to use plastic bags since these bags may break before they enter the analysis lab. The cores are stored at -18 degrees until final analysis. The water samples are equally stored at -18 degrees till final analysis. Stickers should be used for sample identification, no handwriting with a pen.

8. Blank samples

Blank sediment and water samples (obtained outside the dumpsite) must be provided for the analyzing laboratories for calibration and validation of analytical methods. Blank material should be as similar as possible to real samples. However, it should not contain any chemical warfare agents or their degradation products. This must be negotiated with the analyzing laboratory before the start of the sampling campaign.

9. Field documentation

It is recommended that a Sample Log is maintained during sampling to record information for each location including GPS coordinates. For each core the following observations should be entered in the field log:

- Station and core number
- Date and time
- Weather
- Coordinates (lat/long and/or utm)
- Water depth
- Gross characteristics of the surficial sediment: type, colour, obvious odour, biological structures (e.g. shells), presence of debris or oil.
- Vertical changes in sediment characteristics, changes in redox discontinuity
- Penetration depth of the core
- Quality of the core (e.g. fully filled or not)
- Name of the recorder

Task 1.3. Procedures and guidelines for transport and storage of the samples, and sample preparation

1.3.1. Sample transport and storage

Transport

Sediment core samples may be stored upright in the core liner[1]. If core samples are frozen directly after sampling they can be delivered to laboratory without core liner. The clearly labelled plastic bottles which are packet in plastic bags are preferred for sampling. If possible the samples may be divided in subsamples already on board. In that case when sample may be divided in subsamples after the transporting the original sample can be molten and the subsamples can be frozen again. If core samples are transferred without freezing shaking and extreme vibration must be avoided.

New clean plastic bottles must be used. Enough clean sampling equipment must be reserved. The same equipment is only used for one sample. Storage bottles are tightly closed and sample information (ie. the sampling coordinates, depth of sampling place etc.) are clearly and permanently marked.

The concentration of warfare agents in samples may be very different. The safety measures should be planned for highest concentration of warfare agents so the maximum safety can be reached.

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[1] *EPA: Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual p.4-13.*

Storage

Recommended storage time for extractable organics and pesticide type organic chemicals is 7 days before extraction and 30 days after extraction[2]. The storage time can be longer. In VERIFIN tests the storage times could be extended to more than one year without remarkable loss of chemicals found at Baltic Sea samples. It should be noted that some oxidation of sulphur and arsenic-containing chemicals may occur during longer storage. These oxidation products have been already included in the lists of analytes in Table 1 under Task 1.4.

The storage temperature of sediments is recommended to be +4 °C or preferably < -18 °C[2]. The storage conditions should be achieved as quickly as possible after sampling. In VERIFIN the sediment samples are stored at -18 °C and biological samples at -85 °C.

Safety during transport and storage

It is recommended to pack the samples so that if any accident happens the samples are not damaged and spread to the environment. The active carbon containing tightly closed containers should be used. The information of contents, ownership and safety labels (Council Directive 67/548/EEC and CLP-Regulation (EC) No 1272/2008) should be permanently and clearly marked. If samples are transported and stored as samples (not scheduled chemicals), the declarations for OPCW are not needed. In case there are any doubts concerning the declarations or need to declare, the OPCW Declaration Branch should ne contacted.

1.3.2. Sample preparation for the instrumental analysis

As discussed under the sampling procedures the samples should be received at the analyzing laboratory as frozen in a plastic bottle. The sample should contain the pore water. It is not recommended to start the analysis from a freeze-dried sample as all volatile components would have been lost in this type of sample.

At the beginning of the analysis, the sample should be left to fully thaw and then properly mixed. A portion of the sample should be taken for analysis and the remaining sample immediately re-frozen. The analysis portion is then centrifuged to separate the sediment and the pore water. This pre-handling stage is shown in Figure A.

It should be noted that the water content of different sediment samples may vary considerably. Therefore, it is difficult to give accurate amounts for used sediment and pore water samples. It should always be checked that the amount of the remaining sample is enough for the planned analyses.

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[2] *EPA: Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual p.4-4 Table 4-1.*

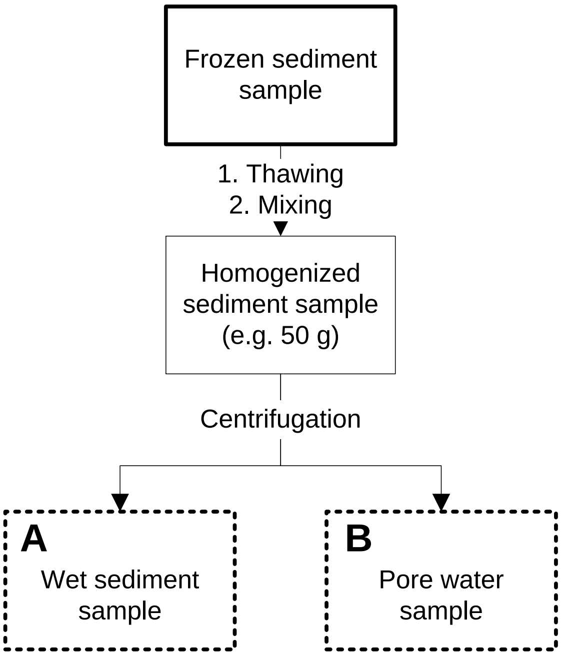

Figure A. *Pre-handling of the received sediment sample.*

<u>Sample preparation of wet sediment</u>

Several portions should be taken from the sediment sample obtained by centrifugation. These portions are analysed using different methods as shown in Figure B.

The first portion is extracted using a non-polar solvent such as dichloromethane (DCM). Part of this extract is analyzed as such and part after derivatization with propanethiol using a gas chromatograph–mass spectrometer (GC–MS). The directly analyzed extract will contain any intact agents present in the sample and the derivatized extract will contain most of the arsenic-containing target chemicals as thiol derivatives.

The second portion is extracted using a more polar solvent such as acetonitrile (ACN). Part of this extract is analyzed as such and part after oxidation using a liquid chromatograph–mass spectrometer (LC–MS). The directly analyzed extract will contain any hydrolysed or naturally oxidized agents and the oxidized extract will contain most of the sulfur and arsenic-containing target chemicals in their oxidized forms.

The third portion will be used for measurement of the dry-matter amount in the wet sediment sample. This can be done by drying the sample e.g. in an oven or in a freeze-dryer. This information is required for reporting the dry weight results.

A laboratory performing organic analyses only would perform only the task related to portions 1–3.

The last portion 4 should be used for heavy metal analyses. The sample preparation will have to be selected based on the available analysis method. Typically, the sample preparation includes digestion and/or extraction steps. Depending on the analysis method one technique may be enough to cover all analytes, but in some cases several parallel methods have to be used.

A laboratory performing heavy metal analyses only would perform only the task related to portions 3–4.

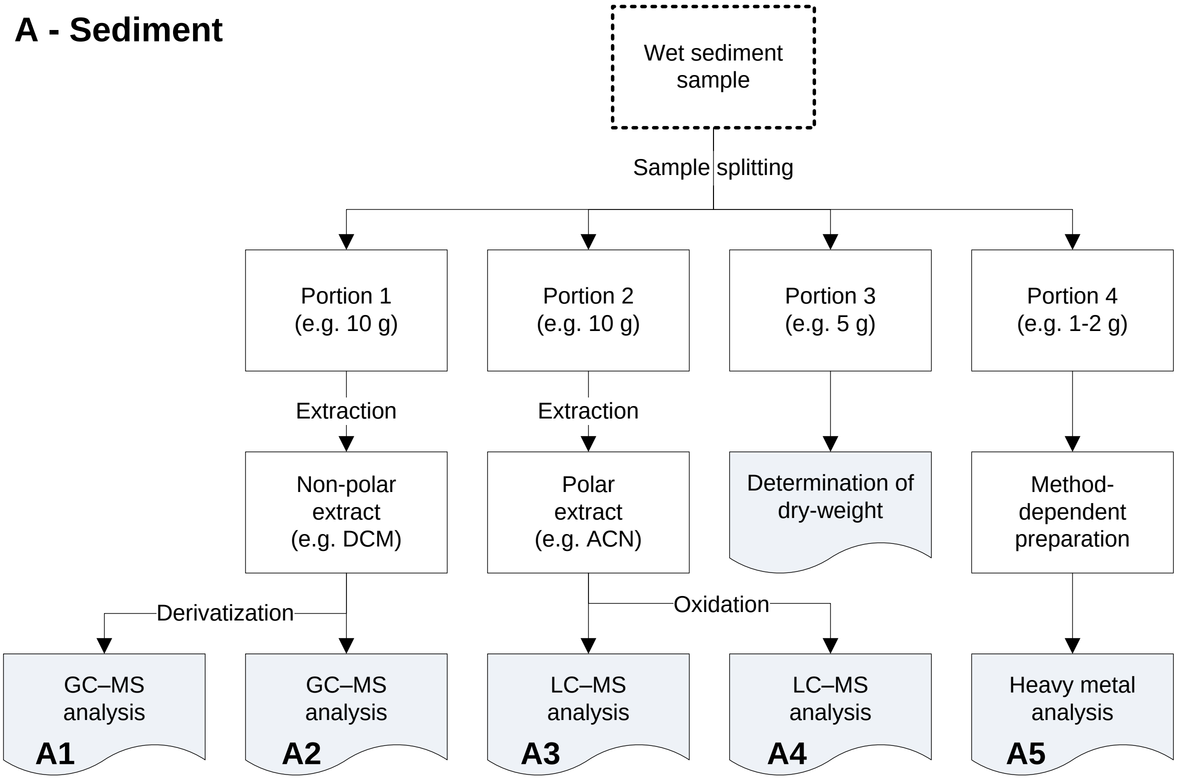

Figure B. *Preparation of sediment samples for analysis. The fractions A1 through A5 are analysed.*

Sample preparation of pore water

Also, the pore water sample has to be divided in several portions for analysis as shown in Figure C.

The first portion is extracted using a non-polar solvent such as dichloromethane (DCM). This extract is handled similarly to the DCM extract of the wet sediment sample and analyzed using a GC–MS.

The second portion has to be cation-exchanged before LC–MS analysis to remove ions from the pore water. After this the sample is handled as the ACN extract of the wet sediment sample and analyzed using an LC–MS.

A laboratory performing organic analyses only would perform only the task related to portions 1–2.

The last portion 3 should be used for heavy metal analyses. As in the case of sediment samples the preparation of the sample will depend on the selected analysis method.

A laboratory performing heavy metal analyses only would perform only the task related to portion 3.

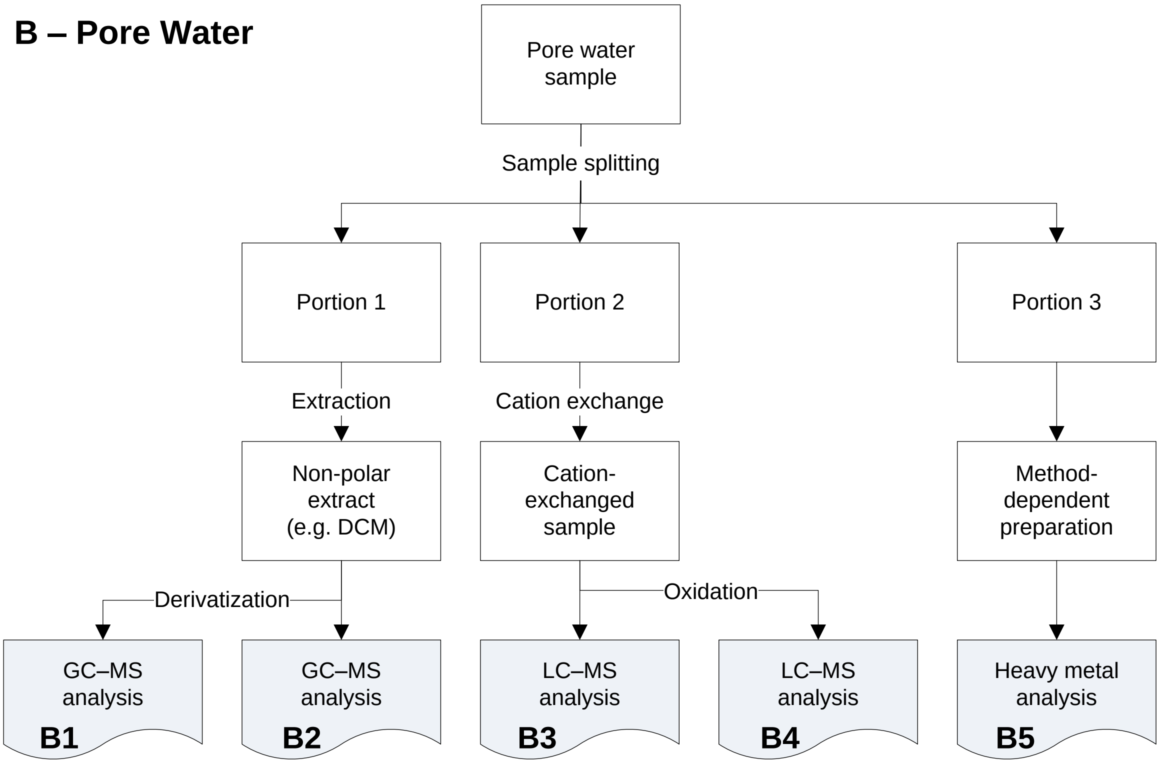

Figure C. *Preparation of pore water samples for analysis. The fractions B1 through B5 are analysed.*

Derivatization and oxidation of sample fractions

All samples will be analysed intact using both GC–MS and LC–MS. In addition to this, samples are analysed on GC–MS after reaction with propanethiol[3,4]. This reaction will convert most of the degradation or oxidation products of arsenic-containing target chemicals to their propanethiol derivative, which are volatile and, therefore, analyzable by GC-based techniques. The oxidation used for LC–MS samples will enhance the ionization of both arsenic and sulfur-containing chemicals [4].

It should be noted that the concentrations measured and propanethiol derivatization or oxidation are always containing the sum of derivatized related chemicals, which have been converted into one single derivative.

Additionally, it should be noted that natural oxidation may occur in sediment samples and that the oxidation reaction will convert all degradation products of an arsenic-containing chemical into one form.

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[3] *John Aasulf Tørnes, Aase Mari Opstad, Bjørn Arne Johnsen, "Determination of organoarsenic warfare agents in sediment samples from Skagerrak by gas chromatography-mass spectrometry", Sci. Total Environ., 356 (2006) 235–246.*

[4] *Tine Missiaen, Martin Söderström, Irina Popescu, Paula Vanninen, "Evaluation of a chemical munition dumpsite in the Baltic Sea based on geophysical and chemical investigations", Sci. Total Environ., 408 (2010) 3536–3553.*

Blank, calibration and control samples

In addition to the actual sample, other samples are required for the analysis procedure:

1. Blank samples are prepared similarly to the actual samples, but from sediment material from an area known to be free of contamination by the target analytes.
2. Calibration samples are prepared by spiking blank samples with analytes. These samples will be used to create the calibration curves for the analytical methods.
3. Control samples are prepared by spiking blank samples with analytes. The control samples will not be used as calibration points, but to verify the correct performance of the analytical method.

As can be noticed from the above, a considerable amount of blank sediment will be needed for preparation of these samples. This material should be supplied by the sampling team(s).

Conclusion

Based on the gathered information the recommended analysis procedure based on both GC and LC-based techniques enables the analysis of all selected target chemicals. Based on the capabilities of the selected analytical laboratories and the agreed analytical techniques the sample preparation may vary from the one presented here.

Task 1.4. Practical recommendations for sampling and sample preparation

Detailed recommendations (including costs involved) regarding the sampling positioning are at this moment not yet possible due to the uncertainty of the method that is to be used. As discussed in sections 1.1.9 and 1.1.10 the most likely options are (1) the system using a diver and heavy load, and (2) the system using a diver with communication cable. The latter can be done e.g. using a Smart Tether communication system which is estimated at roughly 20.000€. Diver positioning is probably best done using a GAPS USBL system. The cost of such a system is estimated at roughly 150.000€. Recently however a GAPS system has been acquired by VLIZ (Vlaams Instituut voor de Zee), and is made available free of charge for the scientific community.

In-situ tests should be carried out to determine which positioning approach is best suited, and most efficient for the Paardenmarkt. As was the case in the past, it seems most appropriate to have the diving and sampling operations carried out by the Belgian navy, in view of their experience with scientific diving and also their long experience with chemical warfare sampling.

The sediment samples should be divided and frozen on-board to be sent to the analytical laboratory immediately after the cruise. The samples should be kept frozen before and during transport.

The packing materials should be tested for the used cooling material, especially if dry ice is to be used. It is of utmost importance that the containers containing samples possibly contaminated with chemical warfare agents are not broken or damaged during the transport.

It has been noted that the sample composition changes if the samples are kept in room temperature during transport (e.g. increase in the amount of oxidized chemicals). Additionally, it has been speculated that bacteria present in the sediment may have some effect on the unfrozen samples.

Several companies are capable of transporting frozen samples from Belgium to other EU countries. At least the following companies based on their service description can send temperature controlled samples:

- DHL (to whole Europe)
- TNT (to whole Europe)
- FedEx (delivers dry ice packages within Europe excluding certain coutries, such as the Baltic area)

There may also be local companies who handle the pick-up of a ready sample. One such company is General Logistics Systems Finland (GLS Finland), which would arrange a package anywhere in Europe and deliver to Finland.

When laboratories responsible for analysis have been selected (see section 2.2), the companies capable of temperature controlled transport should be asked for offers of the sample transport.

Task 2.1. Procedures and guidelines for chemical analysis of the samples

In Task 1.3 procedures and guidelines for transport and storage of the samples, and procedures for sample preparation were described. Recommended sample fractions and analysis methods for chemical analysis of chemical warfare agent (CWA) related chemicals and explosives are given in Table 1. Sample fractions refer to those given in Task 1.3.

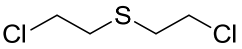
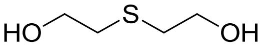
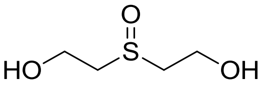
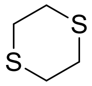
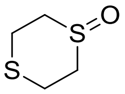
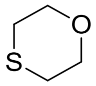
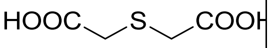
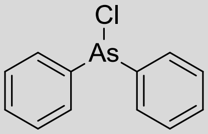
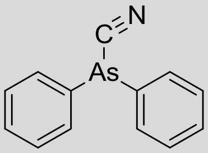
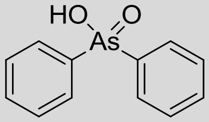
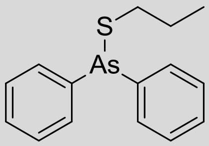
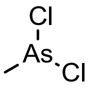
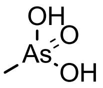
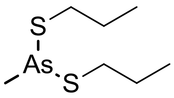
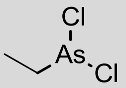
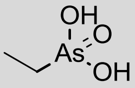
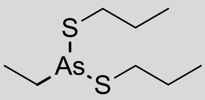
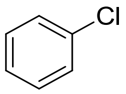
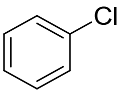
It is recommended that the laboratory/laboratories selected to perform the analyses have a quality system (preferably an accreditation) for the analysis tasks at hand. Additionally, is should be remembered that laboratories may need permits to handle chemical warfare agents and/or explosives required as reference materials.

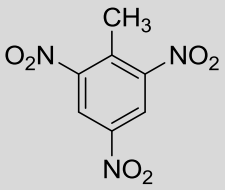
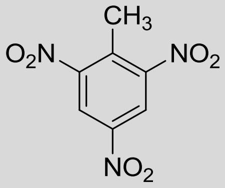
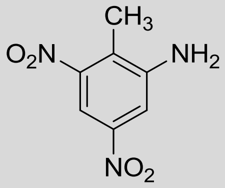
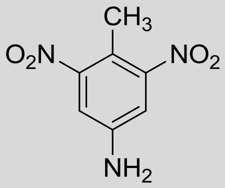
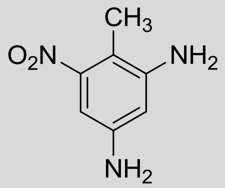
2.1.1. Analysis of chemical warfare agents related chemicals and explosives

Target analytes and the analysis methods

The chemical weapons dumped in the Paardenmarkt area contain many different types of chemical warfare agents (CWA). It is not possible to analyze some of these in environmental samples as they would decompose to chemicals which would not be distinguishable from chemicals from natural sources. Table 1 summarizes those chemicals selected for analysis of CWA-related chemicals and explosives. It should be noted that also one explosive, namely TNT was selected as an analyte as it would be present in both conventional and chemical munitions.

Table 1. *Selected target chemicals and suitable analysis methods*

Original chemical		Target chemical		Analysis method	Sample fraction
Sulfur mustard		Thiodiglycol		LC–MS	A3/B3
		Thiodiglycol sulfoxide		LC–MS after oxidation	A4/B4
		1,4-Dithiane		GC–MS	A2/B2
		1,4-Dithiane 1-oxide		LC–MS after oxidation	A4/B4
		1,4-Oxathiane		GC–MS	A2/B2
		Thiodiglycolic acid		LC–MS	A3/B3
Clark I & Clark II	 	Diphenylarsinic acid		LC–MS after oxidation	A4/B4
		Diphenylpropyl-thioarsine*		GC–MS after derivatization	A1/B1
Methyl-dichloro-arsine		Methylarsinic acid		LC–MS after oxidation	A4/B4
		Methylbis(propyl-thio)arsine*		GC–MS after derivatization	A1/B1
Ethyldichloroarsine		Ethylarsinic acid		LC–MS after oxidation	A4/B4
		Ethylbis(propyl-thio)arsine*		GC–MS after derivatization	A1/B1
Chloro-benzene		Chlorobenzene		GC–MS	A2/B2

Original chemical	Target chemical	Analysis method	Sample fraction
2,4,6-Trinitro-toluene 	2,4,6-Trinitro-toluene (as original chemical) 	LC–MS	A3/B3
	2-amino-4,6-dinitrotoluene 	LC–MS	A3/B3
	4-amino-2,6-dinitrotoluene 	LC–MS	A3/B3
	2,4-diamino-6-nitrotoluene 	LC–MS	A3/B3

* derivative; not present in samples

Selected sample preparation and analysis methods given in Table 1 are suitable for analysis of large number of target chemicals thereby reducing costs of individual analysis. Both qualitative and quantitative analysis is possible from selected sample fractions given in Task 1.3. Either gas chromatography-mass spectrometry (GC–MS) or gas chromatography-tandem mass spectrometry (GC–MS/MS) is recommended for volatile samples as well to those analytes which are volatile after derivatization (e.g. propylthiol derivatives). Liquid chromatography-tandem mass spectrometry (LC–MS/MS) is optimal for water soluble, hydrophilic analytes. The two proposed derivatization methods, oxidation with hydrogen peroxide and derivatization with propanethiol, derivatise both the intact warfare agents and their degradation products. Therefore, the results obtained using derivatization are always the sum of all chemicals. This procedure is decreasing the number of analytes and thereby reducing analysis costs.

The target concentration limit of quantification of chemical warfare agents for sediment and aqueous samples (pore water and near-bottom water) is in the range of 10–50 ppb (µg/kg dw) depending on the chemical. For explosives 100 ppb (µg/kg dw) would be sufficient for limit of quantification.

Identification methods

Both of the identification methods, GC–MS and LC–MS, should be used to search for the target molecules in either selected ion monitoring (SIM) or, if MS/MS instruments are available, selected reaction monitoring (SRM) mode. These methods allow the required sensitivity for the analysis. The SRM would also increase the selectivity and most likely the signal-to-noise ratio, S/N (sensitivity), by reducing the background noise. The ions and reactions will depend on the instrument and the analysis method. The method should be developed and optimized using reference material for each of the target chemicals. It is also important to test the method using samples spiked in blank sediment extracts to take the actual background into account in the selection of the run conditions.

To guarantee the correctness of the identification, at least two ions or reactions should be used for the identification of each chemical. An ion ratio should be calculated for these ions/reactions and it should be compared to the ratio calculated for a reference chemical preferably run at similar concentration level. In order to be acceptable, the ion ratios should be within the limits defined by the European Community (EC) criteria shown in Table 2.[5]

Additionally, the retention times of the chemicals identified in the samples should match those of the reference chemicals. According to the EC criteria,[5] the GC retention times should be within 0.5 % and LC retention times within 2.5 % of the reference values. Additionally, to guarantee satisfactory chromatographic separation, the retention times must be at least twice the void volume of the used column.

The target limit of quantitation (LOQ) for the analytical methods should be aimed at 10 to 50 µg/kg dw (dry weight). The data for the quality control samples and the calibration samples should be reported to show the actual performance of the method. The presented data should include at least:

- mean on the measured values
- error (in %) of measured value compared to spiked amount
- standard deviation (SD) of the measured values
- relative standard deviation (SD/mean in %) of the measured values

The following run sequence (or similar) is recommended for the experiments to establish a satisfactory control of quality:

1. Column performance test (used to verify the general performance of the instrument)[6,7]
2. Blank sample (blank sediment extract)
3. Calibration samples (spiked blank extracts, preferably six levels)
4. Blank sample (blank sediment extract)
5. Samples (e.g. 10 samples)
6. Control sample (spiked blank extract, e.g. 50 pg/µl)
7. Blank sample (blank sediment extract)
8. Samples (e.g. 10 samples)
9. Blank sample (blank sediment extract)
10. Calibration samples (spiked blank extracts, preferably six levels)
11. Blank sample (blank sediment extract)
12. Column performance test

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[5] *Commission Decision of 12 August 2002 implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results (2002/657/EC), Official Journal of the European Communities, 2002, 45 (L221) 8–36.*

[6] *A recommendation for a GC–MS test mixture can be found in V. Häkkinen and M. Söderström, "Gas chromatography–electron ionization/mass spectrometry" in P. Vanninen (ed.) "Recommended operating procedures for analysis in the verification of chemical disarmament, 2011 Edition", University of Helsinki, Finland, 2011, pp 235–245.*

[7] *Recommendation for LC–MS test mixtures can be found in R. Read, R. Black, U. Hakala and P. Vanninen, "Liquid chromatography–atmospheric pressure ionization/mass spectrometry" in P. Vanninen (ed.) "Recommended operating procedures for analysis in the verification of chemical disarmament, 2011 Edition", University of Helsinki, Finland, 2011, pp 282–294.*

Table 2. *Maximum permitted tolerances for relative ion intensities using a range of mass spectrometric techniques. (from ref. 5)*

Relative intensity (% of base peak)	**EI-GC-MS (relative)**	**CI-GC-MS, GC-MS^n LC-MS, LC-MS^n (relative)**
> 50 %	± 10 %	± 20 %
> 20 % to 50 %	± 15 %	± 25 %
> 10 % to 20 %	± 20 %	± 30 %
≤ 10 %	± 50 %	± 50 %

Conclusion

It is recommended to use both GC–MS (or GC–MS/MS) and LC–MS/MS instruments to enable efficient and accurate analysis of the target analytes. The actual combination of the sample preparation and the instrumental methods have to be selected and optimized based on the analytical laboratory's capabilities.

It is also recommended that the analytical laboratory should have at least a quality system covering the type of analysis they are performing, while an accreditation is preferable. Laboratories may also need permits to handle the chemical warfare agents or explosives used as reference materials

2.1.2. Heavy metal analyses

The sea-dumped munitions contain several heavy metals, which pose a possible environmental risk. Additionally, many of the chemical warfare agents contain arsenic.

Considering the large number of targeted heavy metals (Table 3), major attention was paid to the efficient combination of analysis methods, i.e. how well the methods cover the given metals. The reported limit of detection and limit of quantitation of the methods were also evaluated for quantitative and qualitative analysis.

Table 3. *Selected target metals*

Aluminium	Al
Arsenic	As
Cadmium	Cd
Chromium	Cr
Copper	Cu
Iron	Fe
Mercury	Hg
Nickel	Ni
Lead	Pb
Zinc	Zn

Based on the literature review[8] there are no agreed European standards of metal levels in river or floodplain sediments, but assessments on the metal levels in soil[9] as well as in dredged sediments and pore water[10] have been made. Most of the applied water and wastewater analysis techniques are based on the methods published in “Standard Methods”,[11] a joint publication of the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF).

In addition, the United States Environmental Protection Agency (EPA), one of the leading authorities on environmental protection analysis, has accumulated significant knowledge on various sample preparation and measurement techniques. EPA has collected the recommended procedures under their web site[12], which can be used as guidance in setting forth acceptable methods for the regulated and regulatory communities to use. In USA these methods are important part in responding to Resource Conservation and Recovery Act (RCRA)[13] -related sampling and analysis requirements.

The EPA publication SW-846, entitled *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,*[14] is an official compendium of analytical and sampling methods that contain also evaluated and approved methods for analysis of heavy metals. According to EPA recommendations, applicable analysis techniques for heavy metals are listed below in Table 4.

Table 4. *Detection/quantitation limits of analysis techniques for selected heavy metals*

	ICP-AES (LOD, µg/L)[15]	ICP-MS (LOQ, µg/L)[16]	FPXRF (LOD, mg/kg)[17]	IDMS, SIDMS (LOD)[18]	FLAA (LOQ, µg/L)[19]	GFAA (LOQ, µg/L)[20]
Al	30	0.1-1.0	-	-	100	-
As	35	“	40	-	-	1
Cd	2.3	“	100	sub µg/L	5	0.1
Cr	4.7	“	150	“	50	1
Cu	3.6	“	50	“	20	1
Fe	4.1	“	60	“	30	1
Hg	17	“	30	“	-	-
Ni	10	“	50	“	40	1
Pb	28	“	20	“	100	1
Zn	1.2	“	50	“	5	0.05

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[8] *N. Milenkovic, M. Damjanovic, M. Ristic, Polish Journal of Environmental Studies, 2005, 14, 781-787.*

[9] *Joint Research Centre, EC; Heavy metals (trace elements) and organic matter content of European soils: feasibility study by European Soil Bureau Scientific Committee, 1999*

[10] *A. Katsiri, M. Pantazidou, I. Damikouka, Ch. Kontogiorgi, A. Tringali, Global NEST Journal, Vol 11, No 4, pp 449-456, 2009*

[11] *http://www.standardmethods.org/*

[12] *http://www.epa.gov/*

[13] *http://www.epa.gov/lawsregs/laws/rcra.html*

[14] *http://www.epa.gov/osw/hazard/testmethods/sw846/index.htm*

[15] *EPA Method 6010C, Table 1; estimated instrumental detection limits*

[16] *EPA Method 6020A, section 1.2; typical range of lower limit of quantitation*

[17] *EPA Method 6200, Table 1; Example interference free limits of detection in quartz sand*

[18] *EPA Method 6800, section 1.1; typical range of lower limit of quantitation*

[19] *EPA Method 7000B, Table 1; lower limits of quantitation in reagent water*

[20] *EPA Method 7010, Table 1; lower limits of quantitation in reagent water*

The table above shows what techniques are in general applicable for heavy metal analysis. Specific sample preparation procedures are needed for sediment before the analysis. Below are summarized the EPA sample preparation methods for specific analysis techniques (see Table 5).

Table 5. *Applicable EPA sample preparation methods for sediment analyses*

Method	3050B		3051A	3052	3060A
Analysis technique	FLAA, ICP-AES	GFAA, ICP-MS	FLAA, GFAA, ICP-AES, ICP-MS	FLAA, CVAA, GFAA, ICP-AES, ICP-MS	UV-VIS, IC, ICP-MS, HPLC-ICP-MS, CE-ICP-MS
Al	X	-	X	X	-
As	-	X	X	X	-
Cd	X	X	X	X	-
Cr	X	X	X	X	X*
Cu	X	-	X	X	-
Fe	X	X	X	X	-
Hg	-	-	X	X	-
Ni	X	-	X	X	-
Pb	X	X	X	X	-
Zn	X	-	X	X	-

*hexavalent chromium only

According to “Standard Methods” recommendations, applicable analysis techniques for selected heavy metals are listed below (Table 6). Hg was not covered by any of the selected techniques.

Table 6. *Selected analysis techniques for target heavy metals applicable for pore water analysis* [21]

	Sample preparation	Detection mode, detection range	ICP-AES[22]	ICP-MS[23]	AA furnace[24]	AA direct aspiration[25]	AA gaseous hydride[26]	AA chelation–extraction[27]
Al	Digestion	Total, mg/L	X	X	X	X	-	-
As	Digestion	Total, mg/L	X	X	X	-	X	-
Cd	Digestion	Total, mg/L	X	X	X	X	-	-
Cr	Digestion	Total, mg/L	X	X	X	X	-	X
Cu	Digestion	Total, mg/L	X	X	X	X	-	
Fe	Digestion	Total, mg/L	X	X	X	X	-	-
Hg	-	-	-	-	-	-	-	-
Ni	Digestion	Total, mg/L	X	X	X	X		
Pb	Digestion	Total, mg/L	X	X	X	X	-	-
Zn	Digestion	Total, mg/L	X	X	-	X	-	-

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[21] *http://www.standardmethods.org/PDF/Total_CWA_Table_NEMC.pdf*

[22] *Standard Methods 22nd Edition, Editorial revisions 2011, Method 3120 B-2011*

[23] *Standard Methods 22nd Edition, Editorial revisions 2011, Method 3125 B-2011*

[24] *Standard Methods, Method 3113 B-2004*

[25] *Standard Methods 22nd Edition, Editorial revisions 2011, Method 3111 B-2011, C-2011, D-2011 or E-2011*

[26] *Standard Methods 22nd Edition, Editorial revisions 2011, Method 3114 B-2011 or C-2011*

[27] *Standard Methods 22nd Edition, Editorial revisions 2011, Method 3111 C-2011*

Conclusion

Based on the gathered information the recommended analysis procedure is sample preparation of the sediment and pore water samples by digestion using e.g. EPA method 3051A or 3052 (or equivalent), followed by analysis using either ICP-AES, ICP-MS, or different AA techniques.

Task 2.2 Practical aspects with regard to the chemical analysis

2.2.1. Recommendations for institutes

In Section 2.1 procedures and guidelines were described for chemical analysis of chemical warfare agent (CWA) related chemicals and heavy metals in environmental samples from the Paardenmarkt. In January 2013, a "Preliminary questionnaire for surveying costs for environmental sample analysis of metals" (VER-PV-0411) and a "Preliminary questionnaire for surveying costs for environmental sample analysis of chemical warfare agents" (VER-PV-0412) were sent to five laboratories capable for metal analysis and to four laboratories capable for CWA-related analysis and explosives from sediment, pore-water and water samples taken (Appendix 1). Institutes, their contact persons including e-mail addresses and respective countries to which the questionnaires were sent are listed in Tables A and B. Institutes were selected based on previous knowledge on their capacity on analysis of metals or CWA related chemicals from environmental samples.

2.2.2. Guidelines for estimated costs involved

Metal analysis

Three out of five laboratories for **metal analysis** gave response to the questionnaire. Status and summary of replies on questionnaire for metal analysis are given in Tables A and C, respectively. Three laboratories gave prices for requested analysis of ca. 10 elements in 10, 20 or 50 samples. DLD Belgium has an agreement with the Federal Public Health, Food Chain Safety and Environment of Belgium to treat all information on the Paardenmarkt confidential, therefore DLD is currently not in a position to present any details, nor estimation of costs as described in the questionnaire.

For element analysis, laboratories use inductively coupled plasma–mass spectrometry (ICP–MS), atomic absorption spectroscopy (AAS) and/or inductively coupled plasma-atomic emission spectroscopy (Table C, metal analysis). These laboratories work under EPA guidelines (although one of the laboratories did not report this in the response to questionnaire). University of Helsinki and IO PAS are capable for analysis of all requested elements. DLD Belgium did not report those, but presumably has capacity for all elements requested, since the standard applied for sample preparation supports this assumption. Reported limits of quantification are given in Table D.

CWA related analysis and explosives

All four laboratories capable for **CWA related analysis and explosives** responded to the questionnaire. Status of replies and summary of replies on questionnaire are given in Tables B and E, respectively. Three laboratories for CWA related analysis gave a tender. VERIFIN, FOI and

Envilytix GmbH gave detailed price and technical information. DLD Belgium did not report those based on the arguments presented above.

For analysis of CWA related chemicals and explosives, most laboratories have methods for sediment and pore-water samples like described in Chapter 2.1. Laboratories use techniques like gas chromatography-mass spectrometry (GC–MS)(VERIFIN, FOI, Envilytix GmbH), gas chromatography-tandem mass spectrometry (GC–MS/MS)(VERIFIN), liquid chromatography-tandem mass spectrometry (LC–MS/MS)(VERIFIN, FOI) and/or liquid chromatography with diode array detector (LC–DAD)(Envilytix GmbH) (Table E, Analysis of CWA related chemicals). Two laboratories, VERIFIN and Envilytix GmbH, reported capacity to analyze all requested target chemicals.

VERIFIN, DLD Belgium and FOI are designated laboratories of the OPCW and have also accreditation from respective accreditation body. These laboratories work under Quality Management system. Envilytix GmbH has special permission to analyze CWA related chemicals and explosives. The methods of all laboratories are based on in-house developed methods and/or Recommended Operating Procedures published in so called Finnish Blue Books.[28,29] Most significant difference of methods is that Envilytix GmbH needs more sample material compared to those needed by VERIFIN i.e. 1 liter of pore-water or water compared to 10 ml of water needed at VERIFIN. FOI or DLD Belgium did not report sample amount needed for analysis.

All replies on questionnaires are given in Appendices 2–7. All replies included short description on sample preparation and analysis methods. All institutes have valid methods for requested analysis.

Conclusion

IO PAS, University of Helsinki and DLD Belgium have capability for metal analysis using EPA standards. VERIFIN and Envilytix GmbH have methods for all requested CWA related chemicals and explosives. FOI has methods for most of requested analytes and DLD Belgium did not report their capability.

It is recommended that if analysis services are needed all laboratories given in Tables A and B are contacted.

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[28] *Rautio, M., Ed.; Recommended Operating Procedures for Sampling and Analysis in the Verification of Chemical Disarmament , 1994 Edition; Ministry for Foreign Affairs of Finland: Helsinki, 1994.*

[29] *Vanninen, P. Ed.;1. Recommended Operating Procedures for Sampling and Analysis in the Verification of Chemical Disarmament , 2011 Edition; Ministry for Foreign Affairs of Finland, University of Helsinki, Helsinki, 2011.*

Table A. *Status of replies of Laboratories to which questionnaires were sent: Metal analysis*

Institute abbreviation	**Institute**	**Contact person**	**E-mail address**	**Country**	**Reply date**	**Appendix**
IO PAS	Institute of Oceanology of the Polish Academy of Sciences	Marta Szubska Jacek Beldowski	szubi@iopan.gda.pl hyron@iopan.gda.pl	Poland	25 Jan 2013	Appendix 2
MUT	Military University of Technology	Stanisław Popiel	spopiel@wat.edu.pl	Poland	no reply	
UH	University of Helsinki, Department of Geosciences and Geography	Juhani Virkanen	juhani.virkanen@helsinki.fi	Finland	14 Feb 2013	Appendix 3
FOI	Swedish Defence Research Agency	Martin Nygren	martin.nygren@foi.se	Sweden	no tender	
DLD	DLD Belgium	Kris Geukens	kris.geukens@mil.be	Belgium	14 Feb 2013	Appendix 4

Table B. *Status of replies of Laboratories to which questionnaires were sent: Chemical warfare agent analysis*

Institute abbreviation	**Institute**	**Contact person**	**E-mail address**	**Country**	**Reply received date**	**Appendix**
VERIFIN	University of Helsinki, VERIFIN	Martin Söderström	martin.soderstrom@helsinki.fi	Finland	15 Feb 2013	Appendix 5
FOI	Swedish Defence Research Agency	Anders Östin	anders.ostin@foi.se	Sweden	15 Feb 2013	Appendix 6
	Envilytix GmbH	Thobias Bausinger	t.bausinger@envilytix.de	Germany	30 Jan 2013	Appendix 7
DLD	DLD Belgium	Kris Geukens	kris.geukens@mil.be	Belgium	14 Feb 2013	Appendix 4

Table C. *Summary of replies on questionnaires: Metal analysi*s

Institute	**Tender**	**Metals**	**Methods**	**Instrumentation**	**Comments**	**Price for 10/20/50 samples**
Institute of Oceanology of the Polish Academy of Sciences (IO PAS)	Appendix 4	Al, As, Cu, Cd, Ni, Cr, Pb, Fe, Zn, and Hg	no information available	ICP–MS[30] AAS TD–AAS (Hg)[31]		1,180/2,124/4,942 €[32] 1,080/2,024/4,792 €[33]
University of Helsinki, Department of Geosciences and Geography	Appendix 5	Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Zn, and Hg.	EPA 3051 standard	ICP–MS according to ISO 17294-2	[34]	700/1,400/3,500 €[35]
DLD Belgium	Appendix 6	no information available	EPA 3051A and 6010B standards	ICP–AES[36]	[37]	No price given

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[30] Some analysis can be performed with AAS instead of ICP-MS, then price is lower

[31] ICP–MS=inductively coupled mass spectrometry, AAS= atomic absorption spectroscopy, TD–AAS (Hg) =thermal desorption atomic absorption spectroscopy (mercury)

[32] Price for 10 elements: Al, As, Cu, Cd, Ni, Cr, Pb, Fe, Zn, and Hg; Al using ICP-MS

[33] Price for 10 elements: Al, As, Cu, Cd, Ni, Cr, Pb, Fe, Zn, and Hg; Al using AAS

[34] Hg is not included in the standard sediment analysis set, but is available.

[35] Price for 10 elements

[36] ICP–AES= inductively coupled atomic emission spectroscopy

[37] An agreement with the Federal Public Health, Food Chain Safety and Environment of Belgium to treat all information on the Paardenmarkt confidential, DLD is currently not in a position to present any details, nor estimation of costs as described in the questionnaire.

Table D. *Limits of quantification for metal analysis*

Element	**IOPAS LOQ**[38]	**University of Helsinki LOQ from sediment samples**	**DLD Belgium LOQ**[39]
Al	1.2 ppm[40]/0.01 ppb[41]	0.5ppb	
As	0.1 ppm	0.072 ppb	
Cu	0.05 ppm	0.13 ppb	
Cd	0.02 ppm	0.023 ppb	
Ni	0.1 ppm	0.17 ppb	
Cr	0.1 ppm	0.15 ppb	
Pb	0.15 ppm	0.011 ppb	
Fe	0.1 ppm	0.5 ppb	
Zn	0.02 ppm	0.13 ppb	
Hg	5 ppt[42]	0.17 ppb	

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[38] *Limit of quantification*

[39] *No information available*

[40] *AAS method*

[41] *ICP–MS method*

[42] *TD–AAS*

Table E. *Summary of replies on questionnaires: Analysis of CWA related chemicals and explosives*

Institute	**Tender**	**Analytes**	**Designation**[43] **Accreditation**	**Instrumentation**	**Comments**	**Price for 10/20/50 samples**
University of Helsinki, VERIFIN	Appendix 7	As requested in the Questionnaire	OPCW designation; ISO 17025:2005	GC–MS, GC–MS/MS, LC–MS/MS[44]		10,500/21,000/47,500 €
Swedish Defence Research Agency	Appendix 8	10 out of 17 requested	OPCW designation; ISO 17025:2005	GC–MS, LC–MS		35,000/50,000/100,000 SEK
Envilytix GmbH	Appendix 9	As requested in the Questionnaire	no designation, no accreditation, special permission to analyze CWA and explosives	GC–MS, LC–DAD[45]		14,696.50/27,923.35/ 62,460.13 €
DLD Belgium	Appendix 6	no information available	ISO 17025	no information available	[46]	No price given

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[43] *Designation for chemical warfare agent analysis, designated laboratory of the Organization for the Prohibition of the Chemical Weapons (the OPCW)*

[44] *GC–MS = gas chromatography-mass spectrometry; GC–MS/MS = gas chromatography-tandem mass spectrometry; LC–MS/MS= liquid chromatography-tandem mass spectrometry*

[45] *LC–DAD = liquid chromatography with diode array detector*

[46] *An agreement with the Federal Public Health, Food Chain Safety and Environment of Belgium to treat all information on the Paardenmarkt confidential, DLD is currently not in a position to present any details, nor estimation of costs as described in the questionnaire.*

Samenvatting

Doelstelling van deze studie is het maken van aanbevelingen met betrekking tot chemische monitoring van de Paardenmarkt. Deze opdracht wil een antwoord geven op volgende vragen:

- Hoe worden de stalen het best genomen?
- Hoe worden de positionering van de stalen, het voorbereiden van de stalen, de staalbewaring en het vervoer van de stalen het best uitgevoerd?
- Wie kan deze stalen nemen, en wat is de geschatte kostprijs ?
- Welke zijn de analysetechnieken die het best worden aangewend voor kwalitatief en kwantitatief onderzoek?
- Wie kan deze analyse uitvoeren, en wat is de geschatte kostprijs?

Voor het onderzoek werden volgende stoffen weerhouden:

- Yperiet en zijn hydrolyseproducten
- Chlorobenzeen
- CLARK I en II en de afbraakproducten
- TNT en zijn afbraakproducten
- Zware metalen (Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb en Zn).

1. Aanbevelingen betreffende de staalnamelokaties

- Tussen 20 en 30 lokaties binnen de vijfhoek.

- Exacte lokaties worden bepaald door de meest recente gradiometrische studie.

- Focus op grote magnetische anomalieën met geringe diepte (= targetlokaties).

- Daarnaast ook kleinere anomalieën en random lokaties.

- Minstens 2 (max. 5) referentielokaties buiten de vijfhoek, op random lokaties.

- Staalnamelokaties veranderen per campagne voor een optimale bedekking.

- Belangrijkste targetlokaties: regelmatige en lange-termijn monitoring.

- Bij positieve resultaten nieuwe staalname op dezelfde plek.

2. Aanbevelingen betreffende de positionering van de staalname

- Vereiste nauwkeurigheid van 1 meter of minder voor de positionering van de staalnames.

- Bestaande poitioneringssystemen zijn veelal akoestisch (long-baseline (LBL), short-baseline (SBL), ultra-short baseline (USBL), GPS Intelligent buoys (GIB)), maar ook niet-akoestisch (m.b.v. tether).

- Van al deze systemen lijkt het USBL-GAPS systeem het meest aangewezen voor de Paardenmarkt. Het is een relatief simpel transpondersysteem met zeer snelle calibratie en sub-meter nauwkeurigheid. Nadeel is de hoge kostprijs (150.000 €). Dit kan echter opgelost worden door het USBL-GAPS systeem van het VLIZ (Vlaams Instituut van de Zee) te gebruiken.

- Een belangrijk probleem blijft het feit dat de duiker zelf niet weet waar hij/zij zich bevindt. Dit laatste is echter van groot belang voor een correcte staalnamepositionering.

- Een duiker navigatiescherm is geen toereikende oplossing. Dergelijke toestellen hebben veelal een lage nauwkeurigheid (>> 1 m). De enige uitzondering hierop is de Shark Marine Navigator, gebruikt voor militare doeleinden, maar dit systeem is extreem duur. Bijkomende nadelen zijn de geringe zichtbaarheid en sterke stroming, en het feit dat een navigatiescherm de bewegingsvrijheid van de duiker bemoeilijkt, waardoor een dergelijk systeem waarschijnlijk niet is aangewezen op de Paardenmark.

- Er worden daarom twee alternatieve oplossing voorgesteld:
  (1) De duiker, met USBL-GAPS transponder, wordt d.m.v. een communicatiekabel met het schip verbonden. Navigatieinstructies kunnen zo worden doorgegeven zodat de duiker de juiste staalnamepositie kan vinden. Het nadeel van dit systeem is dat het niet practisch is bij slechte zichtbaarhied en sterke stroming zoals op de Paardenmarkt.
  (2) De USBL-GAPS transponder wordt bevestigd aan een zwaar voorwerp (bvb cementblok) dat m.b.v. een touw op de bodem wordt neergelaten boven de staalnamelokatie. De afwijking t.o.v. de exacte staalnamepositie kan bepaald worden (bvb 70cm naar het oosten). De duiker gaat via het touw naar beneden en verplaatst de transponder tot de juiste positie. Dit kan eventueel nog een paar keer herhaald worden.

- Het wordt aanbevolen om beide systemen uit te testen op de Paardenmarkt. Dit kan het best gebeuren door de Belgische marine gezien hun uitgebreide ervaring met staalnameoperaties in het verleden. Een correcte prijsrichtlijn voor het nemen van 10-20-50 stalen is daarom op dit moment niet mogelijk.

3. Aanbevelingen betreffende de staalname zelf

- Eén sedimentcore en één waterstaal per lokatie.

- Sedimentcores in plexiglas buizen van 5-10 cm diameter en hoogte van 50 cm.

- Watersample vlak boven de zeebodem, op de exacte lokatie van het sedimentstaal.

- Twee (2) sedimentstalen per core (5 cm dik, resp. op een diepte van 0 cm en 50 cm) - dit dient te gebeuren VOOR het invriezen

- Sediment- en waterstalen worden ingevroren aan boord op -18°C.

- Alle staalnameapparatuur dient uitgebreid gewassen en ontsmet te worden voor en na elk gebruik.

- Duikers en alle personeel dat in aanraking komt met de stalen dienen beschermende kledij te dragen; gasmaskers en chemische detectoren moeten beschikbaar zijn.

- De cores moeten duidelijk gelabeld worden mbv stickers.

- Uitgebreide sample-log dient bijgehouden te worden tijdens de staalname-operatie.

4. Aanbevelingen betreffende vervoer en opslag van de stalen

- Sediment- en waterstalen dienen (best in bevroren toestand) binnen de twee weken vervoerd te worden naar de opslagplaats.

- Indien de stalen niet in bevroren toestand getransporteerd kunnen worden dan moeten schudden en trillingen tot een uiterst minimum beperkt worden.

- Sedimenstalen moeten vertikaal worden vervoerd en gestockeerd.

- Aanbevolen bewaartemperatuur van sediment- en waterstalen tijdens opslag is -18°C.

- Verpakking is zodanig dat geen beschadiging kan optreden (best kleine containers).

- Duidelijke labels m.b.t. inhoud, eigenaar, en veiligheid (EU regels) zijn onontbeerlijk.

- Bedrijven die het transport kunnen uitvoeren in Europa: DHL, TNT, FedEx, GLS (enkel naar Finland).

5. Aanbevelingen betreffende de staalvoorbereiding

- Sedimentsamples worden in 4 porties verdeeld:
    - 1 portie wordt na non-polaire extractie m.b.v. GC-MS getest op (1) intact CWA en (2) As en thiol derivaten
    - 1 portie wordt na polaire extractie m.b.v. LC-MS getest op (1) gehydrolyseerde en natuurlijk geoxideerde agentia en (2) sulfur en As-houdende agentia in geoxideerde vorm;
    - 1 portie wordt getest op droog gewicht;
    - 1 portie wordt getest op aanwezige zware metalen.

- Watersamples worden in 3 porties verdeeld:
    - 1 portie wordt na non-polaire extractie m.b.v. GC-MS getest op (1) intact CWA en (2) As en thiol derivaten;
    - 1 portie wordt na cation exchange m.b.v. LC-MS getest op (1) gehydrolyseerde en natuurlijk geoxideerde agentia en (2) sulfur en As-houdende agentia in geoxideerde vorm;
    - 1 portie wordt getest op op aanwezige zware metalen.

- Blanco stalen worden identiek voorbereid als de andere stalen maar zijn afkomstig buiten de vijfhoek en bevatten zeker géén CWA.

- Calibratie- en controlestalen worden bereid d.m.v. het ‘spiken’ van blanco stalen met CWA. Deze stalen worden gebruikt om calibratiecurves op te stellen en om de juiste performance te verifieren van de analythische methodes.

6. Aanbevelingen betreffende chemische analyse van chemische strijdmiddelen (CWA)

- Beide identificatiemethodes GC–MS en LC–MS dienen gebruikt te worden voor het opsporen van CWA m.b.v. selected ion monitoring (SIM) of (indien MS/MS beschikbaar is) selected reaction monitoring (SRM).

- Minstens twee ionen of reacties zijn vereist voor de identificatie van elke chemische stof. De hieruit berekende ionenverhouding moet vergeleken worden met deze van een referentiestof van eenzelfde concentratie.

- De ionenverhoudingen en retentietijden moeten vallen binnen de criteria opgegeven door de EC.

- De beoogde limit of quantitation (LOQ) moet liggen tussen 10 en 50 µg/kg dw (dry weight).

- Uitgebreide kwaliteitscontrole en calibratie dien te gebeuren m.b.v.
    - het gemiddelde van de gemeten waarden
    - de fout (in %) van de gemeten waarde tov de ‘spiked’ waarde
    - standaard-deviatie (SD) van de gemeten waarden
    - relatieve standaard-deviatie (SD/mean in %) van de gemeten waarden

7. Bevraging van instituten betreffende chemische analyse van chemische strijdmiddelen (CWA)

- Vier instituten werden aangeschreven: VERIFIN (F), FOI (S), Envilytix (D), DLD (B). Alle vier hebben geantwoord.

- VERIFIN (Finland):
    - Alle CWA; technieken: GC-MS, GC-MS/MS, LC-MS/MS
    - Geaccrediteerd (ISO 17025:2005)
    - Prijs (10/20/50 stalen): 10.500 € / 21.000 € / 47.500 €

- FOI (Swedish Defence Research Agency)(Zweden):
    - 10 van 17 CWA; technieken: GC-MS, LC-MS
    - Geaccrediteerd (ISO 17025:2005)
    - Prijs (10/20/50 stalen): 4.200 € / 6.000 € / 12.000 €

- Envilytix (Duitsland):
    - Alle CWA; technieken: GC-MS, LC-DAD
    - Geen accreditatie
    - Prijs (10/20/50 stalen): 14.700 € / 28.000 € / 62.500 €

- DLD (Laboratoria van Defensie, België):
    - CWA: geen info; technieken: geen info
    - Geaccrediteerd (ISO 17025)
    - Prijs (10/20/50 stalen): geen info

8. Aanbevelingen betreffende chemische analyse van zware metalen

- Een Europese standaard voor toegelaten hoeveelheden ontbreekt. De beste aanpak lijkt daarom de richtlijnen op te volgen van het Environmental Protection Agency (EPA) in Verenigde Staten.

- Dit zowel met betrekking tot de detectie- en quantificatielimieten als de aanbevolen technieken voor de analyse van zware metalen (in sediment en poriënwater).

9. Bevraging van instituten betreffende chemische analyse van zware metalen

- Vijf instituten werden aangeschreven: IOPAS (Po), MUT (Po), UH (Fi), FOI (S), DLD (B). Slechts drie hebben geantwoord.

- IO PAS (Institute of Oceanology of the Polish Academy of Sciences) (Polen):
  - Zware metalen: Al, As, Cu, Cd, Ni, Cr, Fe, Pb, Zn, Hg
  - Geen info mbt methode; technieken: ICP–MS, AAS, TD-AAS
  - LOQ: 0.02 – 1.2 ppm
  - Prijs (10/20/50 stalen):
    - 1.180 € / 2.124 € / 4.942 € (ICP-MS)
    - 1.080 € / 2.024 € / 4.792 € (AAS)

- UH (University of Helsinki, Department of Geosciences and Geography)(Finland):
  - Zware metalen: Al, As, Cu, Cd, Ni, Cr, Fe, Pb, Zn, Hg
  - Methode: EPA 3051 standard; technieken: ICP–MS according to ISO 17294-2
  - LOQ: 0.01 – 0.5 ppb
  - Prijs (10/20/50 stalen): 700 € / 1.400 € /3.500 €

- DLD (Laboratoria van Defensie, België):
  - Zware metalen: geen info
  - Geen info mbt methode; technieken: ICP–AES (inductively coupled atomic emission spectroscopy)
  - LOQ: geen info
  - Prijs (10/20/50 stalen): geen info