Networks of miniature sensors

for low concentrations (ppb) of H2S

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Summary

In the face of increasingly coercive legislation, the need for continuous monitoring of pollutant concentration in the air has increased considerably over recent years, driven by health and safety concerns (toxic gases) and odour related nuisance or discomfort. Although gas exposure limit values are generally measured in parts per million (ppm), odour nuisance is measured by the parts per billion (ppb) presence of indicators gases, a concentration that is one thousand times lower.

Industrial players are therefore faced with the problem of measuring very low concentrations of gas (ppb) over a very wide area on a continuous basis, when the laboratory machines generally used for this purpose do not provide continuous data.

The solution tested as part of this study consisted in equipping a wastewater treatment plant with approximately 30 sensors that measure the concentration of reduced sulphuric gases (hydrogen sulphide H2S and methyl-mercaptan CH3SH) every minute. The sensors have a wireless connection to a viewing station with a special human-machine interface (HMI) that gives real-time alerts if any threshold is passed at any point within the plant. It can also be used to check whether the problem identified occurs at the same time every day and therefore requires preventive action to be taken.

Context

Article 2 of the French Law dated 30 December 1996 on air quality and the rational use of energy states that "*any substances introduced into the atmosphere by human activity, whether directly or indirectly, that may have an adverse effect on human health, biological resources or ecosystems, influence climate change, damage material goods or cause* ***excessive olfactory nuisance*** *shall be deemed atmospheric pollution under the terms of this law*."

As such, although no official odour pollution thresholds have yet been defined, the legislator has introduced the concept of limiting odour nuisance. Maximum odour levels have even been indicated by decree for various environmentally-listed installations (ICPE).

The decree dated 2 February 1998 also defines "odour level" or "odour concentration" as the dilution factor required for an effluent to no longer be perceived as odorous by 50% of a population sample. However, this olfactory threshold remains very low and corresponds to concentrations of only a few ppb, particularly as regards reduced sulphuric composites.

Reduced sulphuric composites like hydrogen sulphide (H2S) and methyl-mercaptan (CH3SH) are often found in solid and liquid sewage treatment plants, where organic matter is broken down using anaerobic degradation.

Monitoring

H2S has generally been measured by taking samples in Tedlar® bags or other special containers and analysing them in laboratories using sulphur chemiluminescence detection (SCD), one of the most selective methods for detecting sulphuric gases. SDC is widely used in conjunction with gas chromatography (GC) to detect reduced sulphuric composites like H2S and generally enables readings of between 2.5 to 5.0 ppb. However, taking these readings remains highly challenging, given the reactivity of this type of gas and the low concentration levels to be measured (ppb range). Moreover, this method does not enable continuous monitoring.

Continuous measurement of very low concentrations of malodorous composites is the only way to monitor plant output and anticipate odour nuisance in the local area.

The continuous monitoring solution currently used consists in placing expensive sensors, which can measure a wide range of gases, close to plant emission sources (where concentration is highest) and then modelling emission dispersion according to wind movement. Unfortunately, this approach often gives approximate results (notably because of the different sources used). These are not compatible with the purpose of this study and cannot be used to identify the precise source and dispersion of an emission.

Another solution consists in surrounding a plant with a large number of cheaper, more sensitive sensors that measure only one or two gas families (sulphuric gas, nitrogen, etc.). This enables concentration levels to be viewed directly instead of through modelling, yielding results are both more precise and more reliable.

As such, we decided to implement this solution.

The Cair CLIP sensor

The gas sensors available on the market are based on electro-chemicals or semi-conductors. They are often used in mobile devices to ensure health and safety at work by measuring occupational exposure values in ppm.

However, these sensors are often disturbed by the sudden changes in humidity experienced around tanks, basins, rivers or the sea.

The Cair Clip sensor (Figure 1) was developed to overcome these problems in the following ways:

* Dynamic air uptake (fan unit) that ensures regular air flow towards the sensor and enhances sensitivity,

* A filter that attenuates sudden changes in humidity and therefore protects the sensor from disturbance,

* A precise, reliable electro-chemical sensor that does not need to be recalibrated more than once a year,

* An electronic circuit that can measure nanoampere currents and enables the sensor to be leveraged to its full capacity.

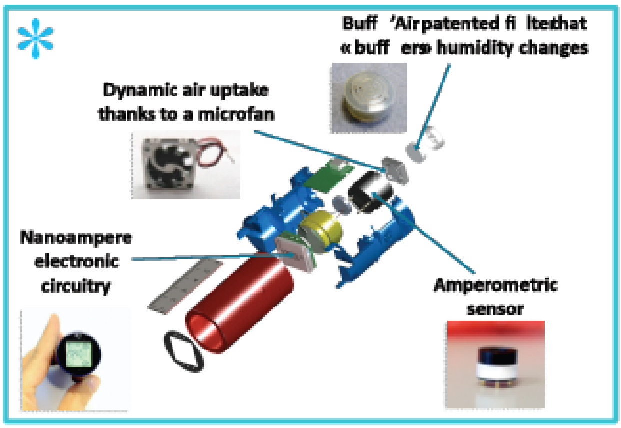

Figure 1: The Cair Clip is a compact device designed to measure low concentrations of H2S and methyl-mercaptan (CH3SH).

The Cairclip can also detect low ppb concentrations of H2S within a shorter timeframe and ensures greater stability when faced with environmental disturbance, requiring no recalibration for a year.

Sensor characterisation in the laboratory

Cairclip sensors are initially calibrated in the laboratory.

The results (Figure 2) show excellent linearity (r2>0.99) and reading sensitivity for low concentrations of H2S (in this case, 0 to 2500 ppb) with a resolution of 4 ppb. Virtually identical performance levels were observed for methyl-mercaptan (CH3SH) readings. This is particularly interesting given that both composites cause significant odour nuisance.

These sensors can therefore detect cumulated concentrations of both these gases in the atmosphere.

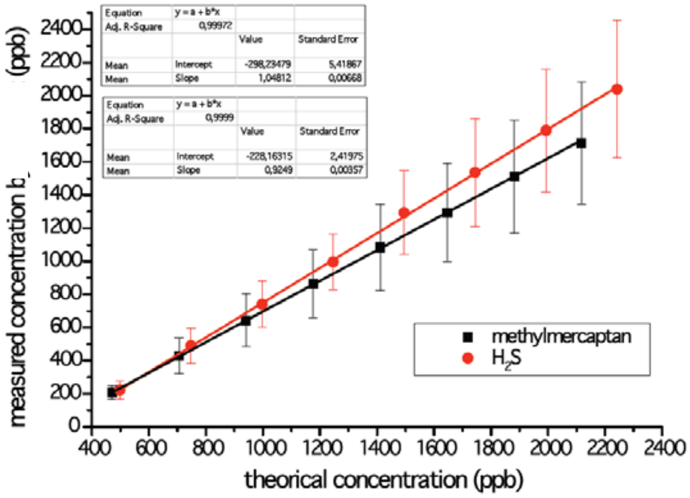

Figure 2: CairClip sensor calibration curve regarding sulphuric composites (in this case, H2S and CH3SH). The "theoretical concentration" is the real-time concentration measured by gas chromatography.

Field trials

In order to facilitate exploitation of the data collected, Cairclip sensors are assembled within a Cairnet that is fitted with a solar panel, back-up battery and wireless communication module.

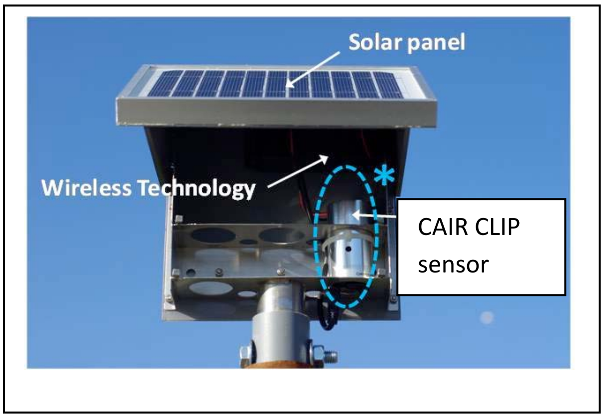

Figure 3: Description of the CairNet and CairClip

A network of 30 CairNet was installed at a wastewater treatment plant in southern France (Figure 4).

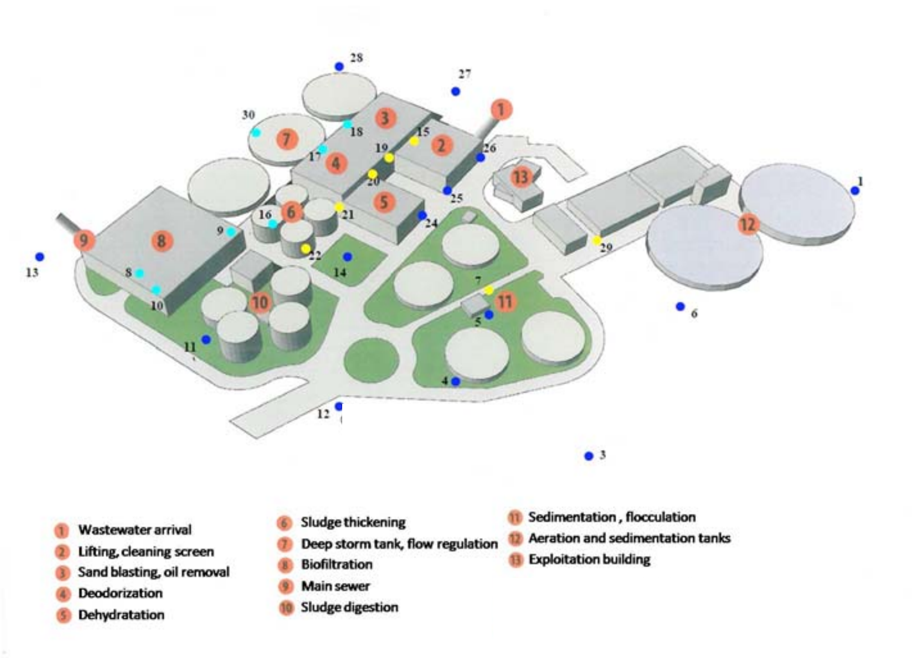

Figure 4: Distribution of 30 CairNet across the wastewater treatment plant

Exploiting the results

The readings taken by the sensors are relayed continuously to a central computer. A man-machine interface is currently being developed that will enable the data to be exploited quickly and easily.

The following example (Figure 5) shows the readings taken throughout the day of 26 May 2010. The results show that the sensors can be used to measure concentrations of H2S (and CH3SH) that vary between very low and 400 ppb across the day. The results also show how odour levels change throughout the day.

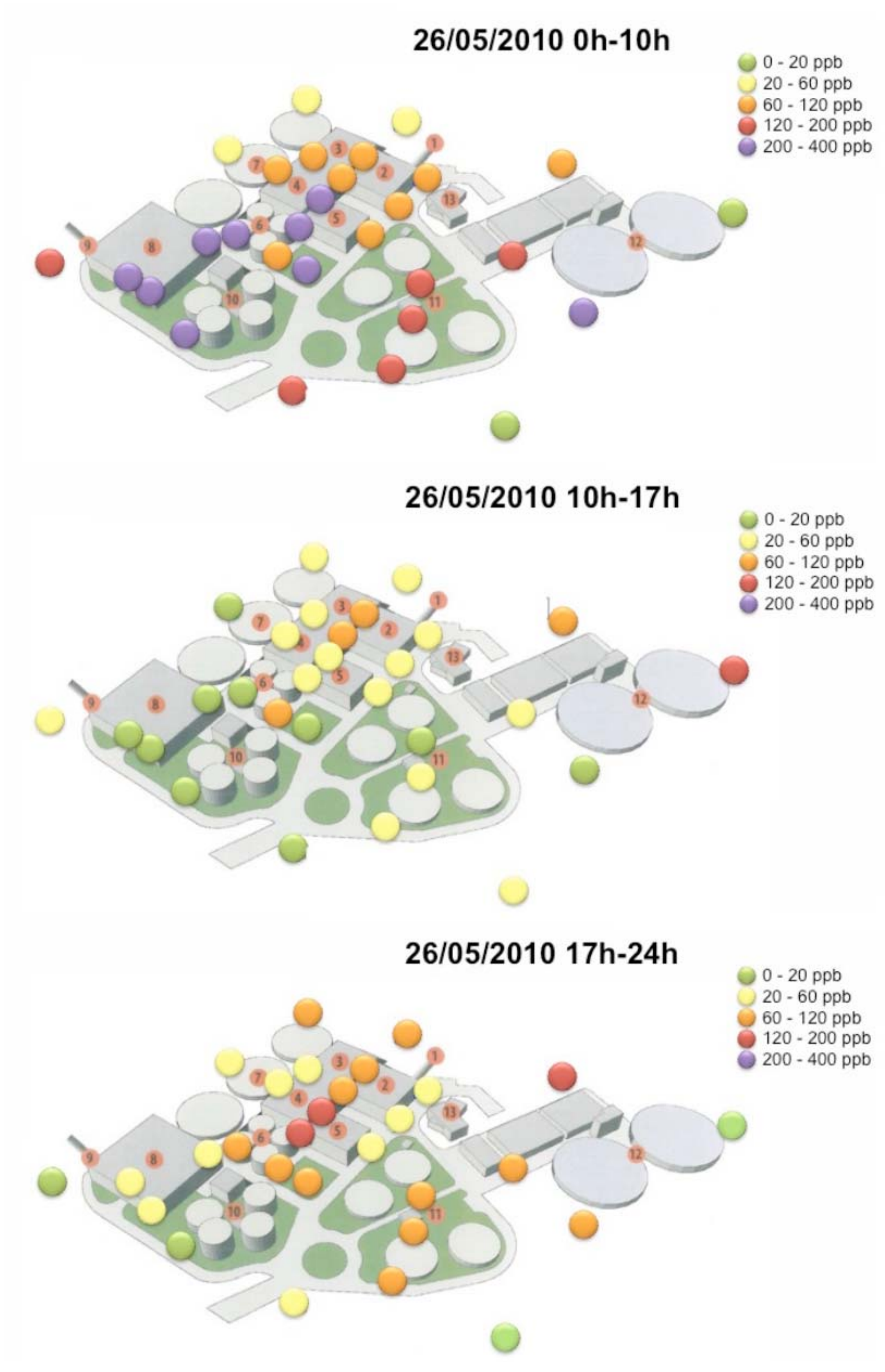

Figure 5: Readings taken at a wastewater treatment plant in southern France, 26/05/2010)

CONCLUSION

This study shows that CairClip sensors perform well when detecting hydrogen sulphide (H2S) and methyl-mercaptan (CH3SH) in real-life situations, and that they can be used to monitor emission sources and occurrence in great detail. As such, it is possible to take partial but precise action with a view to reducing odour emissions.

The next step will consist in combining this new sensor network approach with multiple-source modelling of wind movement in order to obtain greater details of the impact on the surrounding area and possibly forecast odour nuisance.