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Environmental Chemistry Group **www.rsc.org/ecg**

Bulletin

Rare earth oxides – Clockwise from top centre: praseodymium, cerium, lanthanum, neodymium, samarium, and gadolinium oxides. *Credit: PD-USGOV-USDA-ARS/Wikimedia Commons*

In this issue

Rare earths were the focus of this year's **Distinguished Guest Lecture & Symposium** held on March 20th 2013 at Burlington House, London. The 2013 Distinguished Guest Lecture – "Rare Earths and Other Scarce Metals" – was given by **Professor Thomas Graedel**, (Yale University). Other speakers covered materials' criticality, the history and applications of rare earths, and the importance of chemistry innovation in achieving a sustainable use of rare earths and other materials. A meeting report of the DGL & Symposium, and articles based on the presentations at the meeting, may be found on pp 3 to 4, and pp 10 to 20, respectively. This issue also contains the first two ***ECG Environmental Briefs***, a new series of short articles intended as 'how-to guides' on topics of importance in the environmental sciences.

Also

A report including abstracts from a meeting on **Recent advances in the analysis of complex environmental matrices**; and details of upcoming meetings on **Environmental monitoring in the energy sector: exploring parallels between shale gas and nuclear** (September 26th 2013) and **Degradation and toxicity of organic contaminants in the ground** (February 13th 2014).

RSC | Advancing the Chemical Sciences

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Rare earths and other scarce metals – technologically vital but usually thrown away

A report of the RSC Environmental Chemistry Group's Distinguished Guest Lecture and Symposium held on 20 March 2013 at Burlington House, London.

The Symposium was organised by ECG Committee Member Dr Stuart Wagland and chaired by Dr William Bloss (Chair of the RSC Environmental Chemistry Group). There were sixty attendees. The ECG Committee acknowledges support provided by the RSC Environment, Sustainability and Energy Division (ESED), the Chartered Institution of Wastes Management (CIWM) and the Chartered Institution of Water and Environmental Management (CIWEM).

The Symposium was opened by **Professor Andrea Sella (University College London)** with a talk on "Terra Rara – *The Unknown Elemental Sea*", a survey of the origins, uses and chemical nature of the rare earth elements (REEs: scandium, yttrium, and the fifteen lanthanides). He began by emphasising that problems of sourcing REEs were problems of access not abundance. The similar sizes of REE ions means that their separation and purification are difficult; one calculation suggested that with classical nitric acid digestion methods, isolation of a rare earth from a mineral substrate could require some forty thousand recrystallisations. This theme of separation and purification has dominated REE extraction and use ever since Carl Auer von Welsbach used lanthanum and ytrrium oxides in gas mantles in 1886 and in 1903 patented the use of cerium in the 'ferrocerium' flints still in use today. Glassblowing and other technologies created more demand. As further uses emerged, a market for REEs developed and attention shifted to better methods for their isolation.

The first of these is described in a series of papers by Frank Spedding and colleagues in the *Journal of the American Chemical Society* starting in 1947. Their research championed the use of cation exchange resins to purify REEs from the fission products of nuclear reactions. A second change in methodology was introduced following work at Oak Ridge National Laboratory in the 1950s, when resin processes were replaced by more profitable continuous solvent extraction. However, the new techniques had downsides: nitric acid waste, releases of dust concentrate together with hydrofluoric acid, sulfur dioxide, and sulfuric acid, and the production of large amounts of radioactive residues were consequences of the continuous process. This created a concern about the environmental impacts of REE exploitation that continues to this day.

Over the last decade, increasing global demand for REEs means that geopolitical issues are increasing in importance and the exact nature of the developed world's future need for REEs and the threats involved in sustaining supply have become salient. The strategic availability of REEs was covered by **David Merriman (Roskill Information Services)** in his talk on "A Review of Global Supply of Rare Earths". He described how REEs occurred geologically as a consequence of hydrothermal deposition by igneous intrusions and could also be found in sand deposits and in low-cost clays. Before the 1990, the main supplier was Molycorp's Mountain Pass mine in California, but by 2005, China had become responsible for 96% of global rare earth supply. This virtual monopoly did not go unnoticed, and in 2012 there were 200 global exploration projects seeking diversified sources of REEs in Angola, Argentina, Australia, Vietnam, Greenland and Tanzania. China's domination of global REE trading is projected to decrease to 74% in 2015 and 61% in 2018, although China will still dominate the market for heavy REEs. Although growth in production by the rest of the world (mainly US and Australia) is expected, China will continue to dominate until beyond 2018. Urban mining (recycling) will not be a significant source of REEs until large-scale collection is implemented.

REEs are clearly causing a considerable global challenge. One approach to this challenge is to search for substitutes for REEs, as described by **Dr Mike Pitts (Sustainability Manager, Technology Strategy Board)** in his talk on "*Chemistry Innovation in Resource Efficiency*". He referred to REEs as 'Endangered Elements' and argued that future (2050) demand will be insupportable unless design and manufacturing becomes focused on extending the life of manufactured goods and designing-in the capacity for goods to be remanufactured and easily recycled.

Adrian Chapman (Oakdene Hollins) spoke about "*Materials' Criticality – Mitigation Options and Impacts*" in the context of the EU's Strategic Energy Technology Plan, which has classified REEs as critical raw materials. The latter are a group that includes tin, platinum, graphite, fluorspar, magnesium, gallium, and beryllium. A material's 'criticality' is obtained by associating risk with economic importance and the speaker made the point that 'critical' does not mean crisis and that 'criticality' is not linked to geological scarcity; most critical raw materials are abundant but difficult to win. An evaluation of environmental risk is one of the criteria used when a material's criticality is assessed.

Once critical raw materials have been identified there are a variety of approaches possible, including better data collection and dissemination (to improve evaluations of the supply situation); procurement and stockpiling (Japan and the US have adopted this approach); trade and international co-operation (trade is currently dominated by China and this is an inherently unstable situation); design and innovation (substitution); and resource efficiency strategies (better extraction, more recycling, greater impact mitigation and more designed-in capacity for re-use).

As seen previously, when REEs were being purified, chemistry had a role in helping to improve resource use efficiency; increasing this efficiency will make access to lower grade ores financially viable, thereby reducing supply risk. Chemistry also has a role in minimising environmental damage by developing new technologies and pollution mitigation schemes and, since many critical raw materials are by-products of base metals, chemistry can also help to improve base-metal production methods to facilitate access to REE by-products. The speaker suggested that the REE content of manufactured goods could be reduced if the introduction of new materials and new products was accelerated. Due to the technical challenges of reclaiming REEs from waste units (e.g. mobile phones), where they are present in very small quantities, recycling levels are low and recycling has not alleviated the problems of demand.

Assessing 'criticality' takes into consideration supply chain risk, traceability/provenance of supplies, environmental issues, substitution, levels of recycling and process efficiency and Adrian Chapman's paper clearly demonstrated why criticality scores are high for REEs.

Professor Thomas Graedel (Yale University) encompassed many of the symposium's themes in his Distinguished Guest Lecture "*Rare Earths and Other Scarce Metals: Technologically Vital but Usually Thrown Away*". He introduced the concept of Industrial Ecology (IE: the study of material and energy flows through industrial systems) and then illustrated how model systems based on IE can be used to produce whole life cycle analyses of REE usage from ore extraction to disposal, from producers through manufacturers to receivers/users. He made the point that energy costs for extraction, purification, and fabrication of REE containing goods are so high that using once and then throwing away should not be an option. Dissipative uses (such as brake lining manufacture) should also be restrained.

Like the other speakers, Professor Graedel also addressed the 'Challenge of Companionability': the occurrence of REEs in association with large volume metals such as lead, zinc and iron. For instance, if construction decreases, less iron is used, demand for zinc as a galvaniser decreases, less zinc is mined, and less REEs are extracted as a by-product; REE sustainability is thus intimately linked to the demand for other metals that are quite unlike them in terms of properties and use.

In a manner analogous to the EU's critical raw material approach but using a new methodology, the Yale Criticality Project accommodates REE risk factors in a single model of three complementary dimensions, namely supply risk, vulnerability to supply restriction, and environmental implications for human health and ecosystems. Supply risk contains terms to accommodate geology, regulatory threats, political stability, availability of investment etc., while vulnerability to supply restriction includes terms for the availability of substitute materials and/or different sources of REEs and for the effects of external economic impacts on the REE market by events such as those the EU is experiencing currently. Classifying risks into these categories and then assessing all risks to give accumulative scores for each category allows a representation of three composite risk element to be displayed for all REEs at a locus in a three-dimensional criticality space; uncertainty is evaluated using propagated errors from each of the terms contributing to the separate complementary dimensions and represented by a cloud in criticality space.

Professor Graedel closed by summarising his lecture in four main points: Metals occur in geological groups and this strongly influences availability; scarce metal companionability decouples price from production; many REEs are used once and then lost, often by design; and life cycle quantification presents the opportunities that are available to help change our ways. The meeting closed at 17.15 after questions.

(Part Five of *Periodic Tales – The Curious Lives of the Elements*, by Hugh Aldersey-Williams, Penguin Books Ltd, 2012, discusses the early history of REEs under headings such as Swedish Rock, Auerlicht, and Ytterby Gruva. I recommend it.)

LEO SALTER

Cornwall, March 2013

Recent advances in the analysis of complex environmental matrices

A report from a meeting held on Thursday, 28 February 2013 in the Science Suite, Royal Society of Chemistry, Burlington House, London.

About 70 delegates and speakers attended this one-day meeting, which was a joint venture of the Environmental Chemistry Group and the Separation Science Group of the Royal Society of Chemistry and was organised by Dr Roger Reeve from the Environmental Chemistry Group and Professor Graham Mills from the Separation Science Group. The meeting covered analysis of solid, liquid and atmospheric samples, with the common theme of liquid or gas chromatographic separation (LC or GC) with mass spectrometric (MS) detection. The needs of sensitivity and analyte identification in complex matrices were highlighted throughout. Laboratory and field analytical techniques were covered in the presentations.

Graham Mills (University of Portsmouth, Portsmouth, UK) opened the meeting and chaired the first session (Talks 1 and 2). Session Two was chaired by **Roger Reeve** (University of Sunderland, Sunderland, UK) and comprised of three presentations (Talks 3 to 5). The lunch break gave an opportunity for delegates to network, view the literature, and discuss the products on display from the meeting sponsor Agilent Technologies. The four talks in the afternoon session (Talks 6 to 9) were chaired by **Dr Alan Handley** (Head of the Pharmaceutical Sciences Group at LGC and President of Royal Society of Chemistry, Analytical Division).

Probing the water flea's biochemistry – a truly complex but high-information-content environmental sample

Professor Mark Viant (University of Birmingham, Birmingham, UK)

The presentation described the use of metabolomics to investigate the effect of nanoparticles on *Daphnia magna* (**Figure 1**). Can this methodology be used to develop novel information-rich approaches for environmental regulation and to determine the effects of stressors on living organisms? Perhaps genuinely novel mechanisms of toxicity could be discovered. The toxicity of metal oxide nanomaterials is believed to result from oxidative stress. Why use *Daphnia magna*? They are a central component of many ecosystems, are already in use worldwide in aquatic toxicity testing, are easy to culture in the lab with a rapid life cycle, and have genetically identical offspring. There are estimated to be 5000 to 10,000 metabolites in the *Daphnia* metabolome, and determining metabolic responses to stressors is thus an exacting task. The methodology was as follows: *Daphnia magna* exposure to ZnO nanoparticles alongside suitable control samples; extraction of the metabolites; analysis by direct infusion Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometry; followed by signal processing, statistical analysis and metabolite identification with accurate two-dimensional mass spectrometry (MS/MS). More than 4,000 signals were produced from each of 80 spectra to be data-mined. Detailed results of the investigation are to be published later, but the approach is proving to give new biochemical information on the effects of nanoparticles and this could be used inform future studies using more complex test organisms.

Using comprehensive GC (GCxGC) in field devices for atmospheric chemistry

Professor Alastair Lewis (University of York, UK)

The speaker described the development of miniaturised two-dimensional gas chromatography (GCxGC) devices for use in atmospheric chemistry. There is a need for portable

Figure 1: *Daphnia magna.*

Credit: Hajime Watanabe/Wikimedia Commons systems that can easily be used in different field environments. The development of such systems is not a simple task in view of the complexity of the instrument and the need to accurately control flow and temperature. Recent work has involved the use of microfabrication methods borrowed from the electronics industry. The aim is to incorporate all sub-systems in a single module: a lab-on-a-chip. Sophisticated methods are used to etch the silicon wafer to make the capillary GC columns and to either pack or coat the narrow (250 µm) channels with a stationary phase. These chromatographs have for example been used to separate volatile hydrocarbons such as benzene, toluene, and xylenes; however, much more work is needed before these systems can be used routinely in the field.

Analysis of VOCs in complex samples using thermal desorption-GC-MS/olfactory and GC-IMS

Professor John Dean (Northumbria University, Newcastle, UK)

Moving on to studies relating to indoor environments, the speaker discussed issues concerning malodours from washing machines. Are the malodours from the machine or from the laundry itself? If they are from the washing machine, what part is responsible? A number of washing machines were investigated, taking swabs from surfaces and comparing with samples from the fabrics. The volatile organic compounds (VOCs) were analysed by headspace-solid phase micro-extraction (HS-SPME) olfactory GC-MS. Olfactory detection was used to match the chromatographic peak with a particular odour. The most common sources of odours from washing machines were found to be the rubber seal and the sump. Microbial identification from washing machines and laundry gave evidence of contamination of fabrics from the washing machines. Analytical profile index strips and matrix-assisted laser desorption/ionisation-time of flight mass spectrometry (MALDI-TOF-MS) were used in these investigations (**Figure 2**). Most microbes were from environmental sources (i.e. not pathogenic). HS-SPME-GC/MS was used to identify VOCs from bacteria found in the washing machines and fabrics. Ion mobility spectrometry (IMS) may be a possible method for screening VOCs in samples. There is the potential to detect small sulphur- and nitrogen-containing VOCs, but further work is required on authentic samples.

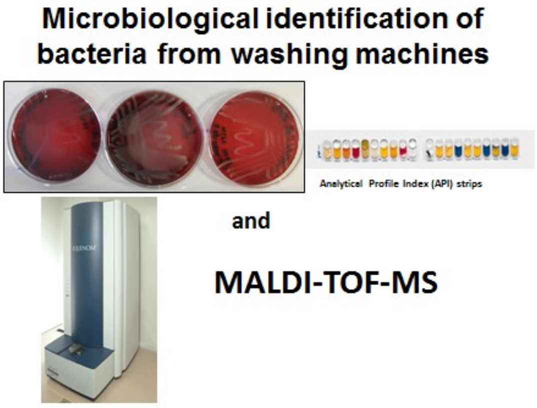


Figure 2: *Identification of bacteria using matrix-assisted laser desorption-ionisation time of flight mass spectrometry (MALDI-TOF-MS) and Analytical Profile Index strips.*

GC-ICP-MS reference methodology to quantify polybrominated flame retardants in environmental waters relevant to the European Water Frame Directive

Dr Panayot Petrov (LGC Limited, Teddington, UK)

The aim was to develop (1) a validated measurement procedure for polybrominated diphenyl ethers (PBDEs) at concentrations specified in the EU Water Framework Directive and (2) advanced analytical methodologies for monitoring pollutant interactions and partitioning between different environmental aquatic compartments. For the first objective, the metrological aim was to quantify six specific PBDEs with a limit of quantification as total concentration below 0.15 ng/L in whole (non-filtered) water. Two separation schemes were devised. The short method (four samples per hour with baseline separation of the target congeners) was suitable for pre-screening. The long method (0.5 samples per hour) showed separation of all 180 congeners. Current instrument detection limits with external calibration are below 1 ng/mL Br and are similar for ^{79}Br and ^{81}Br detection and for quadrupole and sector field instruments. This corresponds to 25 fg/mL Br with a 40,000x preconcentration stage. **Figure 3** shows a typical river water analysis. The second objective concerned partitioning of the pollutants using field flow fractionation techniques. Fractograms were shown of the size distribution in environment water samples and of spiked standards. Ultraviolet/Multi-angle light scattering − inductively coupled plasma – mass spectrometry (UV/MALS-ICP-MS) was used for size and elemental composition. Future prospects are to improve the limits of detection to European Water Framework Directive standards, to use ^{81}Br-enriched samples for quantification in natural water samples, and to employ field flow fractionation in combination with conventional fractionation techniques to better characterise the distribution of PBDEs in water samples.

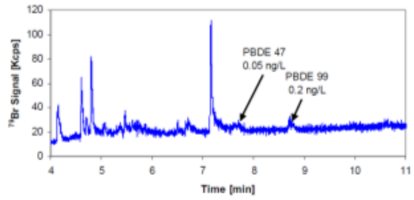


Figure 3: *Chromatogram of the analysis of typical PBDEs found in river water.*

Analysis of non-polar organic compounds in water by GC-MS/MS

Dr John Quick (Severn Trent Services, Coventry, UK)

The presentation described recent work to transfer methods for mainly non-polar compounds from GC-MS and GC-electron capture detection to GC-MS/MS. The aims were to give shorter analytical run times, simplify preparation procedures, achieve specified limits of detection with difficult matrices, and give unambiguous identification of target analytes. Detection in the ng/L range was shown for typical contaminants DDT, HCH and Captam using triple quadrupole MS and was validated on a range of samples (soft/medium and hard potable, borehole and surface waters). Samples were prepared by extraction into *n*-hexane/ ethyl acetate and direct injection into the GC-MS/MS. Two MS transitions were monitored, giving most limits of detection < 2 ng/L. For waste water analysis (typically for polyaromatic hydrocarbons and PBDEs), sensitivity and selectivity become particularly important, as concentrations can be < 0.2 ng/L. Pre-treatment with liquid-liquid extraction was followed by clean-up using an NH_2 solid-phase extraction cartridge, followed by solvent evaporation. Equivalent sensitivity (0.1ng/L) was demonstrated for standards and 0.7 to 2.0 ng/L for real samples. Chromatographic run times were shorter than for previous methods and signal re-processing was simpler. *N*-Nitrosodimethylamine, a probable carcinogen and possible disinfection by-product, was investigated in potable water and sewage effluent. Its low molecular mass can give problems with selectivity. After extraction by solid-phase extraction and solvent evaporation, separation and detection was by GC-MS/MS, monitoring two mass transitions. A good linear range (1 to 20 ng/L) was found. Automated micro-extraction in a packed syringe (MEPS) followed by large volume injection, was also investigated for possible use in rapid screening. A 1 mL sample was loaded onto the syringe in 10 aspiration steps, eluted with *n*-hexane (100 µL), with 25 µL being used for each injection. **Figure 4** shows typical chromatograms.

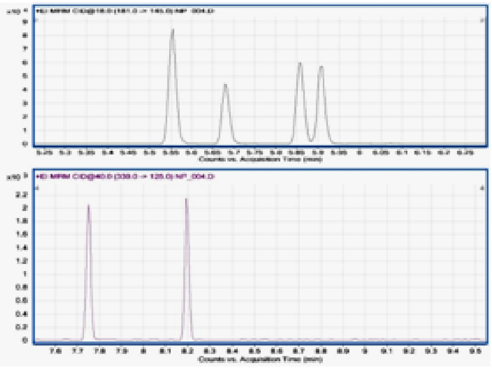


***Figure 4:** Chromatogram of hexachlorocyclohexane isomers (HCHs) (top) and of endosulfans (120 ng/L) (bottom) after microextraction in a packed syringe.*

Enantioselective analysis of chiral pharmacologically active compounds in urban water

Dr Barbara Kasprzyk-Hordern (University of Bath, Bath, UK)

Not only can drugs be chiral, but their physiological effect depends on the enantiomer present. A major route for entry of drugs into the environment is through excretion of the drug and its metabolites. Concentrations of some pharmaceuticals in wastewaters are in the high ng/L range. The enantiomeric composition of a chiral molecule can change throughout its environmental life-cycle. The same molecule may have different activity and toxicity at different stages of the cycle. In the study, pre-treatment of samples by solid-phase extraction was followed by liquid chromatography using either CBH or Chirobiotic V chiral separation columns. Triple quadrupole or quadrupole time of flight mass spectrometric detection was used. A field trial showed the change in enantiomeric composition of drugs along a water course. A major application of the technique is in wastewater profiling, often known as sewage epidemiology (**Figure 5**). The technique has been used to investigate the use of drugs in a specific geographical area and in some cases it may distinguish between legal and illicit uses. Two amphetamines were studied in detail.

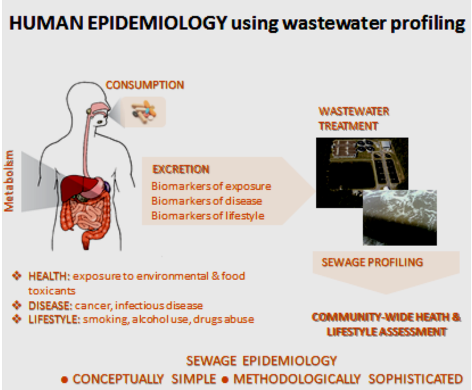


***Figure 5:** Uses of wastewater profiling for human epidemiology.*

Monitoring of cyclic volatile methylsiloxanes in the environment – an analytical challenge

Dr Chris Sparham (Unilever, Sharnbrook, Bedford, UK)

Cyclic methylsiloxanes (octamethylcyclotetrasiloxane, D_4, and decamethylcyclopentasiloxane, D_5) are used in the manufacture of large siloxane polymers and as a base fluid or 'fragrance carrier' for a range of consumer applications. D_4 is no longer used in personal care products but is seen as highly problematic in the environment. Analysis of surface water samples was by headspace-GC/MS, with internal standards being added in the field (**Figure 6**). There were major problems in producing clean blanks. Siloxanes are ubiquitous in analytical laboratories, because septa, columns, vial caps and personal care products from laboratory workers may all contain siloxanes, and analytical operations had to be performed in clean air cabinets. Sediment samples were analysed by large volume solvent injection GC/MS after accelerated solvent or liquid/solid extraction. Biota samples were analysed by purge and trap methods after exhaustive (20 to 24 hour) extraction and introduced into the GC by concurrent solvent recondensation. These analytical methods were sufficiently sensitive for wastewater, sediments and biota, but concentrations in environmental waters were near or below the limit of detection. Passive sampling was investigated to increase the limit of detection, with the specific method chosen to accomodate the high partition coefficents and volatilities of the compounds and to not be a source of D_4 and D_5 contamination. Low-density polyethylene was chosen as the receiving phase. Performance reference compounds were preloaded onto the samplers to provide *in situ* calibration data. The estimated limit of detection for D_4 was approximately 0.1 ng/L in river water.

Figure 6: *Headspace sampling in the field used for measuring volatile siloxanes.*

Characterisation of diesel exhaust particulates by high definition GCxGC-TOF-MS – classification and component speciation for toxicity assessment in humans

Nick Bukowski (ALMSCO International, Llantrisant, Wales)

There is growing evidence that combustion-derived nanoparticles from diesel emissions and diesel exhaust particles cause oxidative stress and inflammation leading ultimately to cell death. No two diesel exhaust particle samples are alike, as shown even by simple fractionation and precipitation. Thermal desorption GC-MS shows the complexity of the samples and need for further separation. Thermal desorption GCxGC-TOF-MS was used in these investigations. Automation of the thermal desorption analysis removed sample preparation and enabled good quality control. The thermal desorption apparatus included sample recollection of the split flow, which allowed repeat analyses to validate analyte recovery and gave an indication of any bias. Cryo-modulation was used between the GC columns but, as running and capital costs are high, preliminary comparisons were later made with flow-modulation. Future work is to translate the cryogenic modulation methods to flow modulation. The chromatograph permitted different gradient profiles between the two columns that are used. Polar–apolar and apolar-polar combinations of columns were investigated. Apolar-polar favoured separation of polyaromatic hydrocarbons; polar-apolar preferentially separated cyclic hydrocarbons and/or olefins. The advantage of the TOF-MS techniques used was a lack of volatility or mass discrimination. The data were analysed by both supervised and unsupervised techniques and correlations made with the NIST library. Unsupervised data mining approaches were found to significantly reduce the burden for the expert data reviewer (**Figure 7**).

Screening for pharmaceuticals and personal care products in effluents and surface water using LC-Q-TOF

Anthony Gravell (Environment Agency for England and Wales, Llanelli, Wales)

Pharmaceuticals in environmental waters include hormones with significant endocrine disrupting effects and antibiotics that could contribute to the build-up of world-wide antibiotic resistance, because many pharmaceuticals are ‘*pseudo*-persistent’. There is a proposal to add some high-use pharmaceuticals to the EU Water Framework Directive Annex X. In order to detect the low concentrations found in effluents and surface waters, a passive sampling technique was used with a polar organic chemical integrative sampler. After extraction, the chromatographic analysis was by liquid chromatography with TOF-MS detection. This instrument was used because it has lower mass uncertainty than quadrupole mass spectrometers. Identification was by scoring bases on accurate mass matching of an isotope (mass match), isotope distribution (abundance match) and isotopic spacing (spacing match). A total of thirty-nine pharmaceuticals and personal care products were found and identified in the final wastewater effluents. They came from a number of therapeutic classes, including beta-blockers, antidepressants, antibiotics and calcium channel blockers. MS/MS with accurate mass provides unequivocal compound identification. A typical matching is shown in **Figure 8** for the product Orlistat (tetrahydrolipstatin) [*N*-formylleucine 1-[(3-hexyl-4-oxo-2-oxetanyl)methyl]dodecyl ester], a pancreatic lipase inhibitor, used as a weight loss aid.

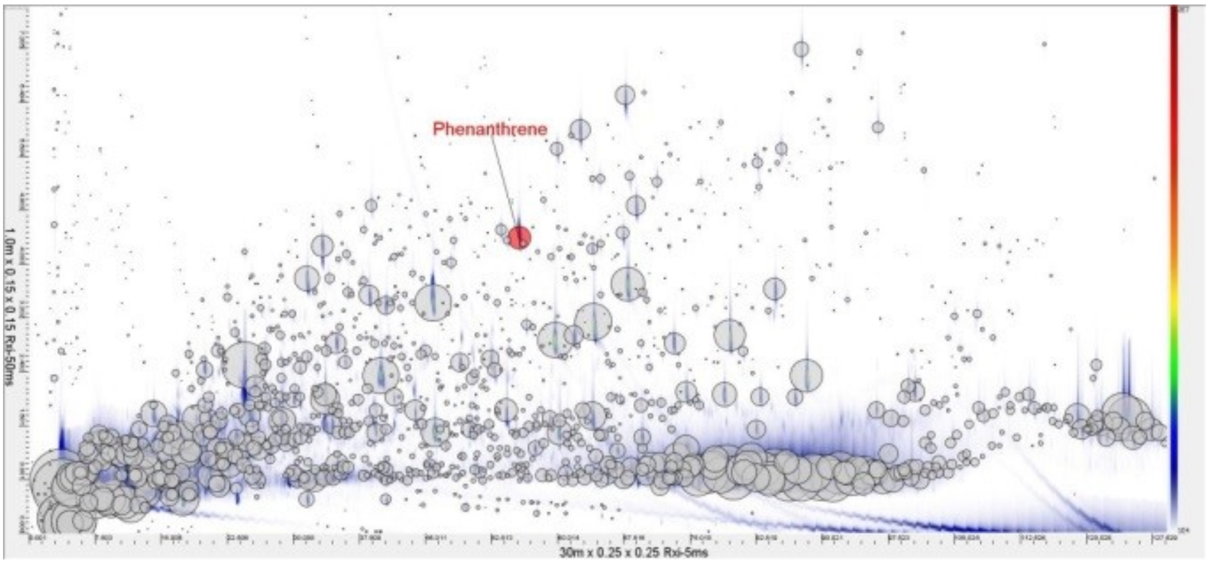
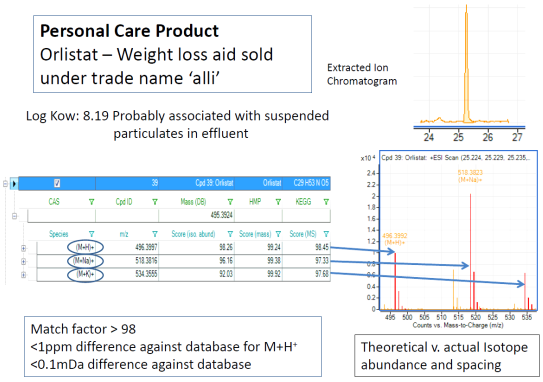


Figure 7: *Unsupervised filtering for oxygenates of a GCxGC chromatogram of a diesel exhaust particulate extract.*



Personal Care Product
Orlistat – Weight loss aid sold under trade name 'alli'

Log Kow: 8.19 Probably associated with suspended particulates in effluent

Match factor > 98
<1ppm difference against database for M+H⁺
<0.1mDa difference against database

Theoretical v. actual Isotope abundance and spacing

Figure 8: *Identification of an analyte by isotope matching.*

The meeting concluded with a general agreement that the event was an overwhelming success, in that so many different matrices and new analytical techniques were covered during the day. Such is the rapidity of advancement in the field that it is hoped that a similar conference will be held in 2015 and will again be jointly organised between the two Interest Groups.

The above abstracts were prepared by **Roger Reeve** and **Graham Mills** based on presentation slides supplied by the speakers. The complete slides are available on: http://www.rsc.org/Membership/Networking/InterestGroups/Environmental/PastEvents.asp

Forthcoming meeting

Environmental monitoring in the energy sector: exploring parallels between shale gas and nuclear

Burlington House, 26 September 2013, 13:30 – 18:00

This half-day science and technology event will consider the current and future role of chemistry in environmental monitoring in the energy sector. The event will centre on a comparison between shale gas, an emerging technique in the UK and the established nuclear sector. It aims to identify common challenges and techniques as well as opportunities for knowledge exchange and collaboration. The event is likely to be of interest to people working on environmental monitoring in the energy sector as well as individuals with wider interests in environmental monitoring techniques including geoscientists, chemists and toxicologists. There is no registration fee but registration is required prior to the event. Please e-mail science@rsc.org for more information.

A review of the global supply of rare earths

Prior to the 1990s, rare earth production from the USA, Australia, and India supported global demand, but this changed when lower-cost Chinese supply became available in the mid-1990s. Chinese rare earth production has since dominated supply, accounting for 97% of global production in 2007. Efforts to reduce China's control of the rare earth element industry since the mid-2000s have resulted in intense exploration and development of rare earth element projects and research into recycling rare earth elements used in magnets and phosphors. Chinese dominance of rare earth elements supply is, however, forecast to continue beyond 2020.

The rare earths elements (REEs) include the naturally occurring lanthanide elements, lanthanum through to lutetium, along with yttrium and scandium. Contrary to their name, their combined crustal abundance is in the region of 120 ppm (1), making them more abundant than copper or lead. Individually, however, certain rare earth elements have much lower crustal abundances. For example, lutetium has an average crustal abundance of only 0.2 ppm (1). The rare earths are typically split into two sub-groups: the light rare earth elements (LREEs), which include lanthanum through to samarium (La, Ce, Pr, Nd, Sm), and the heavy rare earth elements (HREEs), which include europium through to yttrium (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y). Deposits of REEs occur within primary acidic or late-stage igneous rocks such as carbonatites and alkaline intrusives, or as a result of associated hydrothermal activity. Igneous intrusives may be weathered and leached to form clay mineral deposits enriched in REEs, commonly described as ion absorption clays. Secondary placer deposits of heavy mineral may also be enriched in REEs, and deposits formed by weathering of REE-enriched igneous rocks are mined commercially.

Prior to 1990, the USA was the largest producer of REEs in the world from the Mountain Pass mine, California. Australia, China and India were other major producers of REEs during this period. Between 1990 and 1995, Chinese REE production showed strong growth as a by-product of iron ore mining at the Baiyun Obo deposit in Baotou, Inner Mongolia and production from artisanal and small-scale mines in the southern Chinese provinces. The availability of low-cost REEs from China, combined with the increasing cost of meeting environmental standards, caused miners in Australia, India, and the USA to reduce or close operations, strengthening China's position (**Figure 1**).

Chinese dominance of the REE industry peaked at 97% of global production in 2008, as a sharp drop in demand associated with the global economic downturn led to reduced production from non-Chinese producers. Since 2008, increasingly restrictive REE production and export quotas, along with more stringent environmental legislation has caused a number of Chinese producers to close down, reduce production, or consolidate with other producers. In 2010, the Chinese government reduced its export quota (the limit set annually by the Chinese government on a company's exports of REEs out of China) by 40%. This reduction, together with concordant trader speculation, led to rising export premiums, which in turn led to price increases of over 1000% for some LREEs.

An intense period of exploration for REEs during the 2000s led to the initiation of over 300 rare earth projects with varying degrees of viability. Estimated growth in REE demand over the next five years will only support between six and eight new producers. Developing a metallurgical flow sheet (a design plan for processing a material, specifically showing how material is moved around a processing plant from stage to stage) is paramount to a project's success; project size has become less important. A number of rare earth exploration companies have affiliated themselves with specialist chemical or processing companies to provide assistance when developing their metallurgical flow sheet. As the REE market has matured, the ability to extract and process ore is now more important, and projects with established metallurgy have found it easier to gain financing.

The supply of rare earth elements in 2013 will continue to be dominated by China, although production in the rest of the world is expected to increase. New producers such as Lynas Corp. in Australia and Malaysia and SARECO in

Kazakhstan have entered production, and existing producer Molycorp is scheduled to continue to ramp up production. Non-Chinese supply is forecast to reach 24,000t REO in 2013, which, although dwarfed by forecast Chinese production of 105,000t REO, is the highest production of REEs outside of China since the 1990s.

Along with primary mine production, rare earths can be sourced from recycling of materials. Research into recycling appliances containing REEs, including hard disk drives, fluorescent lamps, and NiMH batteries, is on-going. In 2011, Rhodia, a member of the Solvay Group, announced a partnership with materials technology group Umicore, to research recycling REEs from spent fluorescent lamps. In 2012, the company began a new initiative to recycle several hundred tonnes of linear and compact fluorescent lamps a year (2). Recycling of "new scrap" produced during the production process for NdFeB magnets has been widespread for some years now, to increase the efficiency of REE consumption. To date, however, there is no commercial recycling of "old scrap" NdFeB magnets to recover REEs; research into a cost-effective collection and processing scheme is on-going.

The reliance on Chinese production has led to reports highlighting the finite nature of Chinese REE resources, suggesting that current levels of supply may not be sustainable for an extended period. The life-of-mine at some deposits in Jiangxi province have been estimated at less than 15 years, and ore grades at Baiyun Obo operated by China's largest REE producer Baotao Steel Rare Earth Group Hi-Tech Co. are reported to be declining. Extensive exploration within China, however, has identified a further 3.2Mt REO in Fujian province and 0.6Mt REO in Jiangxi province; furthermore, reserves in Guangxi province have been increased to 6.7Mt REO. Though grades at Bayun Obo are reported to be declining, the deposit has a reserve estimate of 28.8Mt REO, enough to sustain mining at current production rates for over 400 years.

In recent years, the rare earths elements have been defined in studies by the British Geological Survey (3), the European Commission (4) and National Research Council (5) to be amongst the group of critical elements. With production becoming increasingly geographically widespread and research into recycling and more efficient consumption underway, the criticality of REEs is expected to be reduced in the years to 2020, although China will maintain its position as the main producing and consuming nation.

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DAVID MERRIMAN

Roskill Information Services Ltd., 54 Russell Road,
London, SW19 1QL, UK

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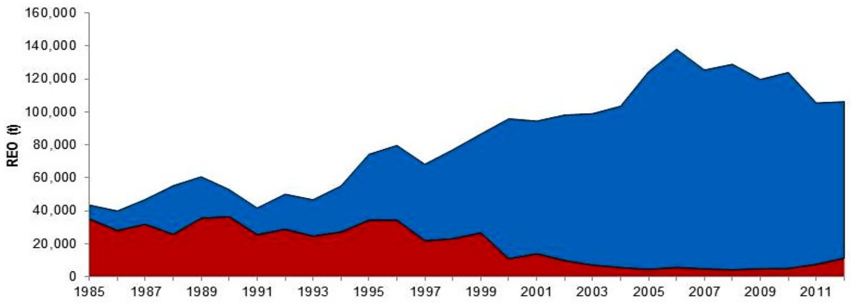

Figure 1: *Historical global production of rare earth elements expressed as tonnes of rare earth oxides (REO) (1985-2012). The transition period highlights when China began to increase REE production while non-Chinese producers reduced output or closed their operations. Blue: Production from Chinese sources; Red: Production outside China. Data sourced from Chinese Ministry of Land and Resources, Chinese Ministry of Industry and Information Technology, Chinese National Development and Reform Commission, China Rare Earth Information Centre, Industry/Company reports and Roskill estimates.*

Chemistry innovation in resource efficiency

How can we provide a good quality of life for all the 9.5 billion people on the Earth in 2050 with the resources of one planet? This is the challenge facing society and will mean huge changes in business models. Increased resource efficiency will rely more and more on the skills of chemists.

Current trends suggest that by 2050, the global population will reach 9.5 billion; in that time span, the middle class is expected to increase by 3 billion, all of whom will aspire to the multitude of labour-saving gadgets that seem crucial to a modern lifestyle (1). Delivering this lifestyle, and the huge savings in embodied and consumed energy required to limit climate change, will require a step change in material efficiency (2). The products and infrastructure that enable our globalised, connected society rely on a largely linear use of natural resources, with limited recycling and reuse of materials. (The UK economy is approximately 75% linear but relies increasingly on imports). Sustainable use of materials is a must.

Materials that are used in vast quantities but that have low energy intensity in production (such as steel and cement) need to have longer in-use lifetimes, particularly given demand for steel is set to rise by 80% between 2010 and 2030 (3). Low abundance materials won at great energy and environmental cost (such as scarce metals) need to be minimised in use and retained in the material economy. For example it takes two million tonnes of solid waste, 691,000 litres of water, and 141 kilograms of cyanide to produce a single kilogram of gold (4). Even for fairly abundant materials such as aluminium, the case for recycling, reuse, or remanufacturing is strong. Avoiding extraction of virgin materials will help manage costs and availability; extraction is predicted to account for 40% of the world's energy use by 2050 (5). Using renewable materials to replace non-renewable resources is also a productive strategy.

The need for resource efficiency in a world of rising material and energy cost and increasing supply risk will drive changes in business models. Resource extraction companies will evolve into resource management businesses and obtain materials from waste streams as well as virgin sources. In many cases the concentration of key resources is already higher in the former than the latter (such as gold in computer scrap and platinum in road sweepings). Suppliers of energy will increasingly become providers of the services that this energy enables, with a focus on efficiency. Manufacturing businesses will shift from making products to managing cycles of materials. This will be driven by retailers and brand owners selling services rather than objects. Waste management companies will exploit their reverse logistics capability and control of material flows to become material managers and key resource providers.

These circular economy business models are already being adopted by forward thinking companies (6). Wider adoption and greater impact will be achieved once chemical scientists and engineers overcome technical hurdles to reducing, replacing, recycling, and remanufacturing materials. Doing this will require a change in mindset: a move away from optimising individual products to considering the whole life cycle of the materials that drive our economy. Perhaps the biggest challenge for molecular scientists is the shift from developing process and products to providing services. As chemists we are trained to make pure materials. Our business models are simple ("sell more of these pure materials"). Yet, customers ultimately buy what a material does, not what it is. The key to a resource-efficient economy is to deliver desired effects as efficiently as possible.

What a waste! *A typical mobile phone contains about 40 different elements, some of which are mined at great environmental cost. A change in mindset is required such that device design minimises such costs and allows reuse and recycling of the materials used.*

Credit: Bakalusha/Shutterstock

Chemistry-using industries are becoming very aware of the issue around long-term availability of resources. Work at Chemistry Innovation Knowledge Transfer Network (CIKTN) (7) since 2008 has sought to raise the idea that elements might be "endangered" and the solution lies in new innovations in chemistry (8). Supply risks for elements are dynamic issues based on geopolitics, technology demands and trends, environmental impact, and economics, but elements will be kept in the economy through clever chemistry (*9*). Following the production of a periodic table of endangered elements, the message started to gain traction and featured in an exhibit at the Design Museum in 2009. In 2010/11, the UK Government's Science and Technology Committee looked into the issue of Strategically Important Metals (10), and an article from Chemistry World (11) was used to brief the minister, David Willetts. The Government response was a Resource Security Action Plan (12). The RSC went on to include supply risk as a factor on its Visual Elements Periodic Table (13), using data supplied by the British Geological Survey (14). Endangered Elements were the topic of a recent BBC Radio Wales Science Cafe programme. The Technology Strategy Board (who fund CIKTN) supported a special interest group on Materials Security (15) in 2011, which looked in detail at the innovation opportunities arising from supply risk of key resources.

Which chemical technologies will rise to the top? Extending the life of materials lies in understanding mechanisms of material failure and will need solutions such as protective coatings and self-healing materials. Recycling is driven by separations science and improvements in metallurgy and alloying. Remanufacturing and reuse of components requires low energy processes for regeneration of parts and one of manufacture using techniques such as 3D printing. Substituting materials needs a deep understanding of structure property relationships to rationally design new materials that deliver the same effects. Chemistry is also vital to exploiting natural, renewable materials. Even extraction of virgin materials will improve with better chemistry for extracting the precious resources we need to thrive as a society.

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MICHAEL PITTS

Technology Strategy Board

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Terra rara – the unknown elemental sea

Lanthanides have very similar chemical properties. Yet, over the past fifty years, different lanthanide elements have come to fill their own niches in technological applications.

The lanthanides or rare earths occupy a peculiar place in the periodic table. Being close to the bottom they seem to sit in its outer reaches, a region seldom reached by school chemistry courses, and indeed often even at undergraduate level. And their peculiarly similar chemical properties – at least in terms of classical chemistry – mean that there was a time when they were looked on with contempt, the great spectroscopist George Pimentel once writing in a textbook that "Lanthanum has only one important oxidation state in aqueous solution, the +3 state. With few exceptions, this tells the whole boring story about the other 14 Lanthanides" (1). Yet at the same time the lanthanides are technologically crucial, each element occupying a specific niche that no other can fill, and their importance has grown over the past five decades. To understand this perplexing situation – similarity of chemistry in spite of extraordinary individuality – we need to understand the lanthanide elements and what makes them tick.

> *"… the lanthanides are technologically crucial, each element occupying a specific niche that no other can fill, and their importance has grown over the past five decades."*

The story of the rare earths goes back about 250 years to the chance discovery of a particularly dense rock by a young amateur geologist, Carl Axel Arrhenius, in a mine near the village of Ytterby (pronounced Ütterbü) on the island of Vaxholm, not far from the Swedish capital Stockholm. Puzzled to have found something that he was unable to identify, he sent a sample to the leading chemical analyst of the day, Johannes Gadolin, who worked at the University of Åbo (now Turku) in what is today Finland. After numerous experiments, Gadolin declared that the mineral must contain a hitherto unknown element, which he named Yttria in honour of the place of its discovery.

The initial report spawned a flurry of work on the dense minerals to be found in the east of Sweden. Over the course of almost 150 years, these minerals were found to contain no fewer than 15 new elements, many of which would be given names associated with the original discovery (scandium, ytterbium, yttrium, erbium, terbium, thulium, holmium, gadolinium). The difficulty lay in their separation, as the elements proved maddeningly similar in their properties. For example, all of them would form precipitates with the same reagents – fluoride or oxalic acid; all would dissolve in mineral acids such as nitric. The differences between them were so small that a complete separation might take as many 40,000 crystallization steps, and their pale colours added to the confusion.

Yet even while chemists expressed general frustration at this unruly gaggle of elements, spectroscopy showed that each had a unique signature, absorbing light of very narrow ranges of wavelengths.

In the lanthanides, the normally accessible outer electrons that give most elements their distinctive chemistry (in this case the $4f$ electrons) are, for quantum mechanical reasons, buried deep inside the core of the atom. The result is that the radius of the atom contracts as you go from the light, early elements (La, Ce, Pr….) across to the heavier, later lanthanides (…Tm, Yb, Lu). It is these size differences that enable separation, although it remains exceptionally difficult. Furthermore, the chemical similarity of the rare earths means that they are found together in mineral deposits, which are typically enriched in either the LRE or the HRE fractions. The rare earths are by no means rare in the earth crust: their abundance significantly exceeds that of the noble metals such as gold and platinum, and even elements we take for granted such as iodine. The problem is not their abundance – it is their chemical similarity.

The Manhattan project provided two solutions to the problem of separation. The first was the deployment at the Ames Lab in Iowa of ion exchange resins, porous beads of a polymer studded with negatively charges. On passing a rare earth solution onto a column of the resin, the ions would travel down the column at rates that depended on their size. This method was very quick, but being a batch process, it did not scale up well. A competing project at the Oak Ridge National Laboratory in Tennessee developed solvent extraction. By adding a binding agent, such as tributylphosphate (TBT), to a mixture of rare earths dissolved in nitric acid, the ions became slightly soluble in kerosene, to an extent that depended on the size of the ion. Thus, by flowing the two solutions past each other, it was possible to separate the ions from each other in large quantities. Today, solvent extraction is the commercial method for separating lanthanides. It is a technically demanding and often messy process that involves the use of large volumes of nitric acid and proprietary binding agents. Environmental and Health and Safety regulation has made separation expensive in the West; this has contributed to the technology moving to China, where costs are lower.

If the rare earths are chemically similar, their electronic structure is another matter. It is the 4*f* electrons that give the ions their remarkable optical and magnetic properties. The mutual interaction of these electrons (there will be between 1 and 13) give the energy levels of the lanthanides a ferocious complexity that tests modern spectroscopic and computational methods to their limit.

> *“The mutual interaction of these electrons […] give the energy levels of the lanthanides a ferocious complexity that tests modern spectroscopic and computational methods to their limit.”*

But this very complexity and distinctiveness provides unparalleled opportunities for applications. The reactivity of the metal cerium toward oxygen has seen it used for well over a century in the alloy ferrocerium that is used in cigarette lighters. The oxide produced – ceria, CeO_2 – has a hardness that makes it ideal for the polishing of glass, jewellery and lenses; it is known simply as “rouge”. Yet this oxide is also the ceramic that helps clean up the exhaust from our vehicles in catalytic converters. The magnetism of the neodymium ion helps to pin the electrons of the iron in the alloy neodymium-iron-boron, giving permanent magnets with an energy product 1000 times greater than in conventional ferrites. Rare earth magnets are to found in electric motors, regenerative brakes, and wind turbine generators. In biomedicine, the fact that the magnetism of the gadolinium ion affects the hydrogen nuclei of water has led to its use in contrast reagents for MRI imaging.

A specific optical transition of the erbium ion produces light that sits at the precise wavelength – 1.3 microns – where transmission of light through optical fibres is at a maximum. Thus erbium is the element that drives much of the optical communications around the globe. The energy levels of Nd, Er, and other rare earths allow the construction of lasers by embedding the ions in a matrix of transparent aluminium/yttrium oxide. If you have a personalized iPad, the letters were probably engraved with one of these. And embedding rare earth ions into other ceramic matrices yields the phosphors for our television screens, our low energy fluorescent and LED lights.

These examples only scratch the surface of the myriad applications to which the rare earths are put. Today we can truly see the truth in the prophetic words of the nineteenth century chemist and spectroscopist Sir William Crookes who became obsessed with these elements: “These elements perplex us in our researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us – mocking, mystifying, and murmuring strange revelations and possibilities” (2).

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ANDREA SELLA

Department of Chemistry, University College London,
20 Gordon Street, London WC1H 0AJ

This article is based on a presentation by Andrea Sella at the ECG 2013 Distinguished Guest Lecture and Symposium held in the Science Room at Burlington House on Wednesday, March 20th 2013. The periodicity and some properties of the lanthanoids are shown on p 20.

Introducing … *ECG Environmental Briefs*

This issue of the ECG *Bulletin* features the first two of a series of *ECG Environmental Briefs.* The series aims to bring concise but authoritative information about aspects of the environmental sciences to members of the Environmental Chemistry Group and to all those with an interest in the chemistry of the environment. *ECG Environmental Briefs* will be published in the ECG *Bulletin* and on the ECG web pages. Please send any comments and suggestions for future *ECG Environmental Briefs* to Dr Martin King

Metal cycles and metal losses

Most uses of metals allow recycling and reuse, but in other cases, losses are almost inevitable. Metal life cycles can help to understand the sources of metal losses and to consider corrective measures, as illustrated by mercury pollution in the New York-New Jersey harbour area. Metal cycles are challenging to develop, especially for metals that are mined and used in small quantities. Close collaboration between materials scientists and resource specialists are required to ensure that criticality (that is, availability in the required amounts) is taken into account in materials development.

As with each human being, each metal has a life cycle. That for metals begins as ores are mined and processed, and continues through product fabrication, product use, and (sometimes) recycling. Imports and exports of ore concentrates, metals, and metal-containing products occur, and losses are inevitable at each transformation. When such a cycle is quantified (generally no easy task), the opportunities for better performance and that challenges that thereby need to be addressed are made much more transparent.

The majority of metal uses are such that recycling and reuse is possible, for example lead in auto batteries, steel in buildings, and copper in wires. In other cases, however, a metal is employed in such a way that its loss is almost inevitable. Examples include molybdenum in lubricants, tin in anti-fouling treatment for the hulls of ships, or zinc as a vulcanizing agent in tyres. Intermediate between these two extremes are uses in which metal could be recovered with increased effort. For a given metal, however, its assignment to one of these classifications is not always obvious.

These points can be illustrated by example, as shown in the nickel cycle for China for 2005 (**Figure 1**). In can be readily seen that imports occur at every stage from mining to manufacturing, that flows into use are some forty-five times greater than the flows out of use (a signal of a rapidly growing economy), and that there exists a moderately well-established recycling chain. In actual fact, a metal cycle analysis is much more detailed than shown here, with every major product flow being determined separately, but **Figure 1** suffices to illustrate some of the benefits and possibilities.

Metal life cycles can also be useful in situations where losses to the environment are known to occur but the source of the losses is undetermined. In a classic study of this type, de Cerreño et al. (2002) set out to identify and minimize mercury pollution in the New York-New Jersey harbor area. They identified the many ways in which mercury was used, and then estimated the inputs to the harbor (Figure 2). Although the error bars for the estimates were wide, it was immediately obvious that dental facilities using mercury amalgams were almost certainly the principal source. With the principal source identified, corrective measures could be considered. By working with dental offices, chairside mercury traps and water filtration systems were installed. The mercury inputs soon decreased and subsequently virtually ceased, as dentists, alerted to the challenge, rapidly adopted ceramic media as a replacement for mercury amalgams.

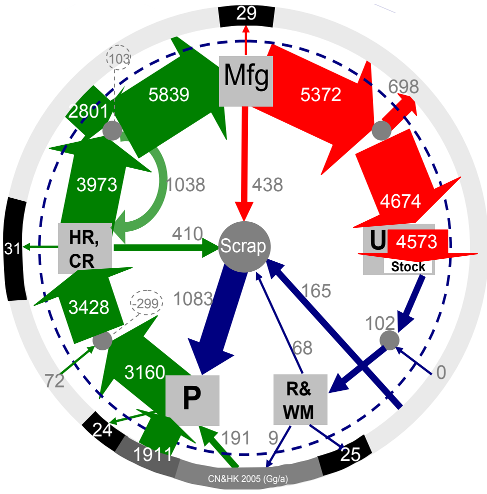

***Figure 1:** The cycle of nickel in China and Hong Kong (combined) in 2005. The flows are given in units of thousand metric tons of nickel per year (Reck et al., 2008).*

The mercury story is dramatic, but also fairly representative of metal cycles in today's world. Cycles are challenging to develop, as data are often not routinely available. Some sort of cycle has been generated for most metals (Chen and Graedel, 2012), but the cycles are well quantified for only perhaps a dozen elements. In the case of metals that are typically mined and used in small quantities, such as indium, germanium, or lutetium, current characterizations tend to be poor or nonexistent. It will not be until cycles across the periodic table are routinely constructed and updated, at different spatial levels, that we will really have a good idea of the degree to which metals are lost during and after use.

Good planetary citizenship would suggest that we can and should do better.

Stocks, flows, and losses of metals are aspects of their “criticality”, a measure of the degree to which metal importance and availability are assessed. Criticality determinations are preliminary at this time, with methodologies still to be finalized and much of the relevant data to be acquired. Nonetheless, preliminary studies (National Research Council, 2008; European Commission, 2010; Nassar et al., 2012) suggest that the biggest challenges likely lie with the scarce metals that are increasingly used in modern technologies. The routine availability of these materials in the desired amounts can no longer be assured, and materials scientists need to build closer collaborations with resource specialists so that materials choices are made in part from perspectives of criticality as well as those of physical and chemical characteristics. Doing so will not ensure that no unsettling issues will arise, but will make such a circumstance much less likely, and will thereby contribute to the robustness of our technological society as a whole.

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T. E. GRAEDEL
Yale University,
New Haven,
CT 06511, USA

This article is based on a presentation by Thomas Graedel at the ECG 2013 Distinguished Guest Lecture and Symposium held in the Science Room at Burlington House on Wednesday, March 20th 2013.

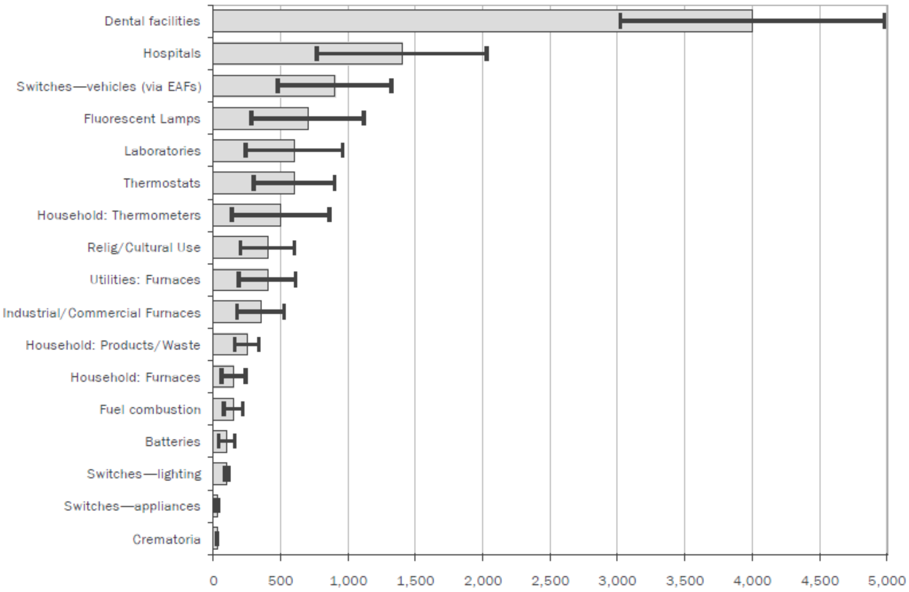

Figure 2: *Estimated losses of mercury to the New York-New Jersey harbor area from identified sources in year 2000 (de Cerreño* et al.*, 2002). The units on the abscissa are kilograms of mercury per year.*

Mind the gap: materials' criticality – mitigation options and impacts

The theme of critical raw materials such as rare-earth elements has been of growing interest to industry and organisations. Concerns over criticality are likely to continue as a result of growing consumption and resource nationalism. The most appropriate mitigation option should be selected depending on the raw material and the application. The chemical sciences can provide solutions and enabling technologies.

Raw materials such as the rare earth elements, indium, platinum and gallium play a vital role in technologies such as flat panel displays, high-strength magnets, batteries, and catalytic converters. These materials are also employed in many "green" applications such as wind turbines, electric vehicles, solar panels, and low-energy lighting. There have been growing concerns over access to many of these raw materials, with the rare earths being the most recent high-profile example. These concerns have resulted in a number of studies to assess the criticality of raw materials. Although there is no universal definition of criticality, many studies combine an indicator of supply risk with another of importance (for example economic impact or importance to a technology) for a given group of materials (**Figure 1**).

These indicators themselves draw on factors such as geographical concentration of supply, end-of-life recycling rates, availability of substitutes, and uses in applications. Criticality is therefore a relative rather than an absolute measure, with assessments comparing materials against each other rather than against a defined baseline. Criticality is not closely tied to geological scarcity in the short term; most of these materials have large reserves, and it is other influences that have an impact on their supply.

Study methods are tailored to the needs of a particular interest group: Some studies take into account a broad range of metals, industrial minerals or, more recently, biotic materials; others assess a specifically chosen set of raw materials of particular interest to a particular market. Studies also rely on a specific context, such as a territory, a group of linked technologies, or materials critical to a business (1). Others include environmental issues within the assessment, either linked to supply risk or environmental impacts.

Despite these diverse interests and approaches, a broad consensus seems to have emerged as to which resources are critical. Analysis of 12 studies by Oakdene Hollins has identified 8 raw materials that are consistently identified in studies of criticality. They are beryllium, gallium, indium, magnesium, tin, tungsten, platinum group metals (PGMs), and rare earth elements. Although these materials present an easy-to-digest list, other materials should not be excluded from consideration, partly because criticality is context-dependent.

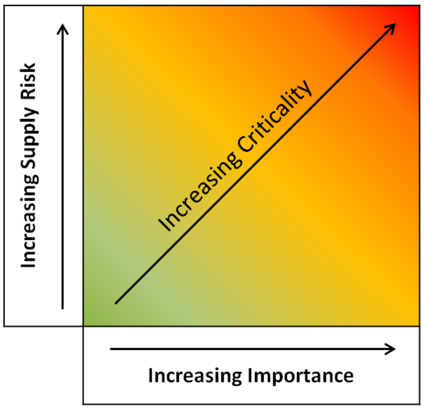

Figure 1*: A two-dimensional criticality matrix combines supply risk with importance.*

Responses

Six types of response can be identified to mitigate the criticality of materials. Different strategies are required depending on the particular material, circumstance, and application. Chemistry and the chemical sciences have a role to play in at least three of these: primary production, design and innovation, and resource efficiency.

Primary production. Improving and diversifying primary production has a key role to play in mitigating supply risk. Metals such as the PGMs, indium, and gallium also have some of the highest environmental impacts per tonne; improvements in primary production could help to reduce these impacts (2, 3). There is a clear role for chemistry in developing technologies to minimise processing losses, provide economic access to lower ore grades, reduce energy usage, and improve separation. In addition, many materials identified as critical are by-products of primary production but are often not separated because their economic value is small compared to that of their carrier metals (4).

Developing new extraction and separation techniques for these metals would increase the attractiveness of by-production to metals producers.

Design and innovation. Chemistry has a large role to play in providing technologies to substitute critical raw materials. Several different substitution strategies exist (**Figure 2** – see p 20). These approaches are necessarily application-focussed, given that the complete substitution of material across all its uses is generally neither possible nor desirable. The Critical Raw Materials Innovation Network (CRM_Innonet), funded by the European Union's Seventh Framework Program (FP7) and coordinated by the Chemistry Innocation Knowledge Transfer Network (CIKTN), aims to identify where priorities should lie (5).

Resource efficiency. Within this category sit options such as recycling, remanufacturing and reuse. Recycling rates of critical raw materials are believed to be very low (6), and where recycling activity does take place it does not necessarily reduce primary consumption.

Not all applications lend themselves to recycling of critical raw materials, either because the materials are present in small quantities or are highly dispersed. For example, many metals are present in small quantities on printed circuit boards. Copper can be and is recovered; however many other metals are lost in the processing due to poor initial separation of components, shredding and then incorporation within other metal fractions or in the slag. There is an opportunity for chemists to develop technical and processing technologies to improve separation outcomes. For example, research into reprocessing rare earth magnets is underway, which has long term possibilities for recovering these materials from wind turbines and electric vehicles. Other strategies such as product remanufacturing and reuse may be more practicable in many cases (7).

Outlook

Concerns over 'criticality' are likely to continue as consumption and resource nationalism grow. The most appropriate mitigation option will strongly depend on the raw material and the application. The chemical sciences can play a central role in addressing these issues. Raw materials criticality has also highlighted broader but related issues, including risks associated with the complete supply chain of products, traceability and provenance of materials, and the environmental impact associated with their production. The chemical sciences also have a role to play in addressing these concerns.

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ADRIAN CHAPMAN
Oakdene Hollins

This article is based on a presentation by Adrian Chapman at the ECG 2013 Distinguished Guest Lecture and Symposium held in the Science Room at Burlington House on Wednesday, March 20th 2013.

Forthcoming meeting – The RSC's **Environmental Chemistry Group** and **Toxicology Group** are planning a joint meeting next year on the **Degradation and toxicity of organic contaminants in the ground**, to be held on February13th 2014 at the Chemistry Centre, Burlington House, London. Full details will be circulated later this year. Suggestions for the content of this meeting and offers to help with its organisation are welcome – please contact *James Lymer*

Dematerialisation	Reducing the quantity of material required for application; e.g. reducing the indium content in indium tin oxide conductive layers
Alternative material	A direct replacement of a material; e.g. replacing graphite anodes with other materials such as titanium based materials.
Alternative system	Substituting a component or part of a system, whilst maintaining the same function; e.g. using alternative motor types in favour of those containing rare earth elements.
Alternative products	Switching to an entirely different product; e.g. substituting one mode of transport with another option such as video-conferencing.

Figure 2: *Substitution strategies for critical raw materials.*

Lanthanum and the lanthanides (lanthanoids) – atomic number; symbol; element name; electronic configuration [M^{3+}]; crustal abundance (ppm)[a]

57 **La** Lanthanum $[Xe]4f^{0}$ 30	58 **Ce** Cerium $[Xe]4f^{1}$ 60	59 **Pr** Praseodymium $[Xe]4f^{2}$ 8.2	60 **Nd** Neodymium $[Xe]4f^{3}$ 28	61 **Pm** Promethium $[Xe]4f^{4}$ 0[b]	62 **Sm** Samarium $[Xe]4f^{5}$ 6	63 **Eu** Europium $[Xe]4f^{6}$ 1.2

64 **Gd** Gadolinium $[Xe]4f^{7}$ 5.4	65 **Tb** Terbium $[Xe]4f^{8}$ 0.9	66 **Dy** Dysprosium $[Xe]4f^{9}$ 3.0	67 **Ho** Holmium $[Xe]4f^{10}$ 1.2	68 **Er** Erbium $[Xe]4f^{11}$ 2.8	69 **Tm** Thulium $[Xe]4f^{12}$ 0.5	70 **Yb** Ytterbium $[Xe]4f^{13}$ 3	71 **Lu** Lutetium $[Xe]4f^{14}$ 0.5

[a] S. R. Taylor, 'Abundance of chemical elements in the continental crust: a new table', *Geochim. Cosmochim. Acta*, 1964, **28**, 1273. Some other values for comparison: Co 25 ppm; Mo 1.5 ppm; Cd 0.2 ppm.

[b] Radioactive; 14 radioisotopes reported.

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ECG Environmental Briefs

Calculating photolysis rates and estimating photolysis lifetimes (ECGEB No 1)

Many chemical species in the environmental sciences undergo direct photolysis. This *ECG Environmental Brief explains* how the rate and typical photolysis lifetime for simple photolytic reaction can be calculated and highlights some common issues. Often the calculation of the photolytic lifetime is enough to decide if a photolytic process should be further studied or can be considered unimportant and ignored.

Chemicals and pollutants in the atmosphere, water and even snowpack may be directly photolysed by solar radiation. It is useful to know how fast this process may be or to calculate a photolysis lifetime (time to decay to $1/e$ of an initial concentration).

Consider a pollutant chemical, A, released to the environment that is photolabile. The pollutant, A, may absorb a photon of solar radiation, $h\nu$

$$A + h\nu \rightarrow \text{products} \qquad (1)$$

The rate of loss of concentration of chemical A, $[A]$ is

$$d[A]/dt = -J[A] \qquad (2)$$

The coefficient, J is dependent on the intensity of solar radiation and the photo-physical properties of chemical A and may be calculated as

$$J = \int \Phi(\lambda,T)\,\sigma(\lambda,T)\,F(\theta,\lambda)\,d\lambda \qquad (3)$$

where Φ is the quantum yield for photolysis of chemical A and σ is the absorption cross-section, both as a function of wavelength, λ and temperature, T. The solar spherical or point irradiance is $F(\theta,\lambda)$. The quantity $F(\theta,\lambda)$ is often termed as the "actinic flux" but this term is often wrong and misleading (*1*). θ is the solar zenith angle. For well-studied pollutants, values of the quantum yield and absorption cross-section data can be found in the scientific literature or publications such as (*2*). The calculation or measurement of spherical or point irradiance can be tricky, however, radiative transfer codes [e.g. (3)] and tables [e.g. (4)] can be used to calculate point irradiances. The quantity, J, is a first-order reaction decay constant, thus the reciprocal of J is a characteristic lifetime (i.e. time τ for the concentration of A, [A] to decay to $1/J$ or ~37% of its initial concentration).

$$\tau = 1/J \qquad (4)$$

Calculation of a value of *J*

As an example of how to calculate a photolysis rate coefficient, J, consider the photolysis of gas-phase ozone in the atmosphere at a temperature of 273K, *i.e.*

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (5)$$

Reaction (5) is an important step in the production of atmospheric hydroxyl radicals responsible for removal of atmospheric volatile organic compounds. The top panel of **Figure 1** plots the absorption cross-section and quantum yield for reaction (5), along with solar point irradiance (for a solar zenith angle of 60° with no cloud, aerosol and an ozone column of 300 Dobsons), as a function of wavelength. The product of the absorption cross section, quantum yield and solar point irradiance (*i.e.* $\Phi(\lambda,T)\sigma(\lambda,T)F(\theta,\lambda)$) is displayed in the middle panel of Figure 1. The shaded area in this panel is equal to the photolysis rate coefficient in equation (3) and be calculated using Simpson's rule or similar. For the example in the figure, the photolysis rate coefficient is $12.1 \times 10^{-6}\ s^{-1}$ and corresponds to a photolysis lifetime with respect to $O(^1D)$ formation of ~23 hours.

Cautionary points in calculating *J*

The calculation of values of J should always consider issues with convolution, whether the calculation is an underestimate, the applicability of the quantum yield, the logarithmic base of the absorption cross-section and the differences between photochemistry and photolysis.

The absorption cross-section, quantum yield and spherical irradiance are all functions of wavelength. These quantities change rapidly with wavelength and for the absorption spectra (especially for gaseous species, such as BrO) may be very structured on the scale of less than 0.1 nm, yet calculations of the photolysis rate coefficients are often performed at 1 to 10 nm resolution. To calculate accurate photolysis rate coefficients, the cross-section must be convoluted to be the same resolution as the point irradiance and quantum yield.

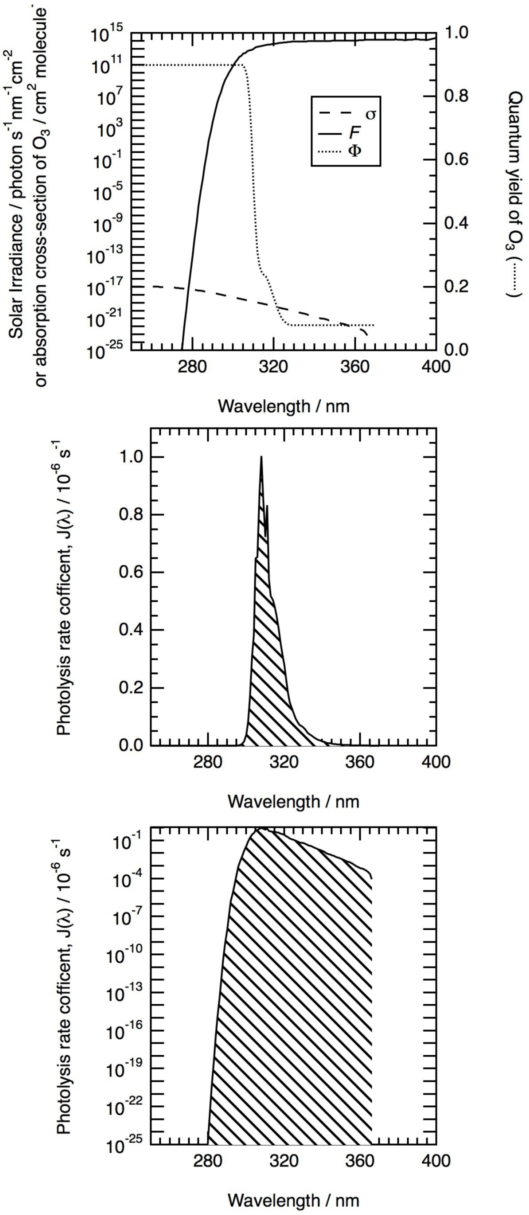

Figure 1: *Calculation of J for photolysis of gas-phase ozone to produce O(^{1}D). No data are available at wavelengths above ~360 nm.*

Many calculations of photolysis rate coefficients are an underestimate. The solar irradiance increases rapidly with wavelength in the UV part of the spectrum, whilst the cross-section and quantum yield often decrease rapidly with wavelength in the same wavelength range (see top panel of Figure 1). The increase in solar irradiation is over many orders of magnitude, whilst the absorption cross-section is rarely measured over two or three orders of magnitude. Thus a long wavelength tail of equation (3) is often missing. The effect is obvious in the bottom panel of Figure 1, which is the middle panel plotted on a logarithmic scale.

Careful reading of the quantum yield in in the literature is needed. The quantum yield can be determined for the number of molecules photolysed (i.e. loss of a pollutant) or as the number of reactive molecules generated. If there is more than one possible product then there will be a quantum yield for each reaction channel. (For example, for the photolsis of nitrate in water there is one quantum yield for formation of nitrite anion and one quantum yield for the formation of nitrogen dioxide.) To calculate the rate of total loss of starting material, photolysis rate coefficients must be calculated for each channel.

For calculation of photolysis rate coefficients, the absorption cross-section should be recorded or converted to the value derived from the Beer-Lambert law using base e as opposed to base 10. Most spectrometers record absorption cross-section as base 10.

Photolysis tends to generate more reactive species as products than the initial reactant and there is often subsequent chemistry between reactant and product that may further remove the initial reactant. Thus it is important to realise that equation (4) is the photolysis lifetime, i.e. respect to photolysis, and not a photochemical lifetime that may be different owing to chemical reaction following the photolysis.

Conclusions

The calculation of an estimate of J and its use in the calculation of the rate of photolysis of a chemical or a photolytic lifetime in the environment is reasonably straightforward, but care should also be taken to make sure an accurate calculation is being preformed. Further information is available in the references; this document is merely an overview to demonstrate that the calculation is facile.

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MARTIN KING
Department of Earth Sciences,
Royal Holloway, University of London,
Egham, Surrey, T12 5NX

ECG Environmental Briefs

Contaminated land (ECGEB No 2)

The UK along with other industrialised nations has a legacy of land that is contaminated with materials from previous use or from naturally occurring sources such as radon gas. This *ECG Environmental Brief* outlines the regulation of contaminated land, focusing on the site investigation and assessment methodology.

Contaminated land management requires an integrated approach from a multi-disciplinary team. It should include chemists who understand the behaviour and toxicity of chemicals in the environment and can evaluate the results of chemical testing analyses based on an understanding of the analytical methods used and the information they provide.

Regulations and regulators

Greenfield land sites are those which have not previously been built on by humans. This includes the greenbelt land around urban environments. In contrast, brownfield land sites are those which have been built on by humans, including waste disposal sites such as landfills, sewage works and reservoirs where no buildings may be present at the surface. Brownfield and Greenfield land that may be contaminated with pollution is dealt with in the UK by two main approaches:

- Part II(a) of the Environmental Protection Act 1990
- Local Authority Planning System

Under Part II(a), Local Authorities are responsible for the inspection of contaminated land and for ensuring that remediation is undertaken where necessary. Local Authorities also maintain a Public Register detailing the regulatory actions that they have implemented. The Environment Agency has a complementary role, for example acting as the enforcing Authority for designated special sites. Contaminated land is also a consideration within the Local Authority planning system. When planning permission is sought for the development of a site, the Local Authority may require investigative work to be completed by the applicant with respect to its contamination potential. The Environment Agency will provide advice to Local Authorities on the risk assessment and remediation of contaminated sites with particular emphasis on the pollution of controlled waters. Planning permission may be granted on the condition that the site is remediated to the satisfaction of the Local Authority depending on the results of any investigation.

The main difference between Part II(a) and the planning system is that in the latter, risks have to be assessed based on the new or intended use of the land, rather than on the existing use, which is a criterion in the Part II(a) regime.

Conceptual model

A risk-based approach is adopted in the assessment of contaminated land. This approach includes the identification of contaminant-pathway-receptor relationships, resulting in the derivation and updating of a conceptual model through various phases of work.

Investigation

Typically, Environmental Consultants are employed to investigate contaminated land sites, e.g. on behalf of a developer seeking planning permission or of the Local Authority assisting with a Part II(a) inspection.

An initial desk study (Phase I) involves the identification of potential sources of contamination, pathways and receptors by assessment of information such as historical plans, geological maps and industrial profiles. A qualitative risk assessment is then performed for the site based on the conceptual model.

If Phase I identifies potentially significant source-pathway-receptor linkages, a site investigation (Phase II) may be carried out to provide quantitative information on the contaminant source, to assess pathways and the risk to the receptors as part of a Generic Quantitative Risk Assessment (GQRA). Phase II involves obtaining soil and/or groundwater samples and submitting them for chemical analysis. Soil and rock samples are obtained by the drilling or excavation of the ground. If concentrations are particularly elevated, a Detailed Quantitative Risk Assessment (DQRA) can be performed. This detailed assessment involves the use of computer models to derive site specific assessment criteria (SSAC) for comparison with contaminant concentrations in soil.

Human health risk assessment

Soil Guideline Values (SGVs) are a type of Generic Assessment Criteria (GAC) published by DEFRA/ Environment Agency. Soil Guideline Values are “trigger values”. Above these levels, soil concentrations may pose a possibility of significant harm to long term human health (**Box 1**).

Soil Guideline Values represent the estimated average daily exposure of a human receptor to a soil contaminant which is equivalent to a minimal risk toxicological value. The two types of toxicology value used are: Threshold (substances where a non-zero, measurable dose produces an adverse effect) and non-Threshold (substances where there is a risk for any dose above zero). Soil Guideline Values are derived for various generic land uses (residential, commercial) using the Contaminated Land Exposure and Assessment (CLEA) model; the latest version of this model is detailed in Environment Agency document SC050021/SR3. SGVs published before 2008 were removed by the Environment Agency in August 2008, with updated values released from March 2009. Soil Guideline Values published between March and July 2009 include BTEX, arsenic, mercury, nickel and selenium.

Box 1: An example of an SGV

Arsenic generally forms organic and inorganic compounds, with the most common valence states being -3, +3 or +5. Arsenic's commercial applications have been in decline for some time due to its toxicity. Potential sources in the environment include non-ferrous metal smelting, pesticides and wood preservatives. Inorganic arsenic compounds are considered carcinogenic both *via* inhalation and ingestion, and it is classed as a non-threshold contaminant. The CLEA model is used to estimate the average daily exposure from arsenic in soil which is equivalent to its non-threshold toxicity value. This is reported as a soil concentration that represents a minimal risk to long term human health known as a SGV.

Inorganic arsenic SGVs are as follows:

Residential:	32 mg/kg dry weight
Allotment:	43mg/kg dry weight
Commercial:	640 mg/kg dry weight

Risk assessors can derive their own Generic Assessment Criteria using the CLEA model software package, as detailed in Environment Agency (EA) document SC050021/SR4. Land Quality Management (LQM) and the Chartered Institute of Environmental Health (CIEH) published their updated Generic Assessment Criteria in July 2009. Volunteers from environmental consultancies working with the Contaminated Land: Applications in Real Environments (CL:AIRE) and the Environmental Industries Commission (EIC) published Generic Assessment Criteria for a range of contaminants in January 2010. Both the LQM/CIEH and EIC/CLAIRE based Generic Assessment Criteria projects have aimed to complement the EA Soil Guideline Value programme.

The CLEA model software can also be used by risk assessors to derive SSAC values as part of a DQRA to compare with contaminant concentrations in soil. The model is limited in the number of pathways considered and can only be used to assess the risk to long term human health from contaminants in soil.

Groundwater and surface water

The Environment Agency Remedial Targets Methodology; Hydrogeological Risk Assessment for Land Contamination provides a tiered structure for assessing the risk to groundwater and surface water receptors from soil and/or groundwater contamination. The methodology involves increasingly complex equations to derive remedial targets in soil from Level 1 to Level 4 and in groundwater from Level 2 to 4; data requirements and assessment complexity increase with each level. The remedial target becomes less conservative at increasing levels as more site specific data is used. The remedial target is based on reducing the soil and/or groundwater concentrations at the contamination source to concentration that poses no significant risk to receptors, e.g. rivers, public drinking water abstractions or the sea.

Remediation

Remediation is usually required when the results of the GQRA or DQRA indicate that contaminant concentrations pose a significant risk to critical receptors. In general, remediation requires design, implementation of remedial treatment, and validation monitoring following remedial works. Remedial activities may require planning permission and/or other environmental permits. There are many remediation techniques that can be applied either in-situ where treatment is carried out beneath the ground or ex-situ where the ground is excavated and treated at surface.

Glossary

BTEX	Benzene, toluene, ethylbenzene and xylene
CIEH	Chartered Institute of Environmental Health
CL:AIRE	Contaminated Land: Applications in Real Environments
CLEA	Contaminated Land Exposure Assessment
DQRA	Detailed Quantitative Risk Assessment
EA	Environment Agency
EIC	Environmental Industries Commission
GAC	Generic Assessment Criteria
LQM	Land Quality Management Ltd
SGV	Soil Guideline Value
SSAC	Site Specific Assessment Criteria

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JAMES LYMER
Wardell Armstrong